

NASA/TM—2016-218946



# Hardness and Microstructure of Binary and Ternary Nitinol Compounds

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## Acknowledgments

A sincere thanks to Peter J. Bonacuse, Joy A. Buehler, Jesse R. Bierer, Ankesh Madan, Jordan D. McCrone, Dr. Quynhgiao N. Nguyen, Edward L. Pang, Dr. Richard B. Rogers, and Walter A. Wozniak for all of their technical assistance and to Drs. Othmane Benafan, Anita Garg and Ronald D. Noebe for numerous technical discussions. This work was funded by the NASA's Transformational Tools and Technologies Project.

This report contains preliminary findings,  
subject to revision as analysis proceeds.

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## Abstract

The hardness and microstructure of twenty-six binary and ternary Nitinol (Ni-Ti, Ni-Ti-Hf, Ni-Ti-Zr and Ni-Ti-Ta) compounds were studied. A small (50g) ingot of each compound was produced by vacuum arc remelting. Each ingot was homogenized in vacuum for 48 hr followed by furnace cooling. Specimens from the ingots were then heat treated at 800, 900, 1000 or 1100 °C for 2 hr followed by water quenching. The hardness and microstructure of each specimen was compared to the baseline material (55-Nitinol, 55 at.% Ni – 45 at.% Ti, after heat treatment at 900 °C). The results show that eleven of the studied compounds had higher hardness values than the baseline material. Moreover, twelve of the studied compounds had measured hardness values greater 600HV at heat treatments from 800 to 900 °C.

## Background

The Ni-rich intermetallic nickel-titanium compound known as 60-Nitinol began being developed for engineering applications nearly 50 years ago but was shelved because it was difficult to machine to tight tolerances due to warping (Ref. 1). More recent work at NASA has shown that this material has great potential for aerospace bearing applications but dimensional distortion during processing has remained a recalcitrant issue (Refs. 2 to 4).

The heat treatment process required to harden 60-Nitinol to acceptable values for bearing applications requires the material to be heated above the solvus at approximately 1050 °C and then rapidly quenched (Ref. 5). This heat treatment, if above the solvus temperature, is designed to render the material single phase in its B2 cubic austenitic form. Due to the high concentration of Ni, however, a metastable  $\text{Ni}_4\text{Ti}_3$  phase will precipitate during cooling (Ref. 6). This fine phase precipitation hardens the material. The goal of the rapid quench is primarily to prevent formation of the metastable  $\text{Ni}_3\text{Ti}_2$  phase or the equilibrium  $\text{Ni}_3\text{Ti}$  phase. These phases do not induce hardening but actually lead to softening in the material by reducing the amount of metastable  $\text{Ni}_4\text{Ti}_3$  phase present (Refs. 6 and 7). Even so, the high level of residual stresses created in a part after undergoing the drastic heat treatment just described is the likely cause of the observed dimensional distortion with this material. The purpose of this investigation was to determine if the solvus temperature of Ni-rich nickel-titanium compounds could be reduced with certain ternary additions, thereby reducing the severity of the heat treatment and, likewise, the occurrence of dimensional distortion. This determination will be made by measuring the hardness of the material and percentage of second phase present in the microstructure.

## Experimental Procedures

Nickel and titanium pellets, tantalum powder and hafnium and zirconium chips were purchased from commercial sources. The purity of each material was certified by the supplier as listed in Table 1. Only the impurities at levels of 1 ppm or greater are reported. It should be noted that Zr typically accompanies Hf because they are found together in nature and are difficult to separate due to their chemical similarity (Refs. 8 and 9).

Twenty-six Ni-rich binary intermetallic Ni-Ti compounds and ternary Ni-Ti-Ta, Ni-Ti-Hf or Ni-Ti-Zr compounds (listed in Table 2) were produced by vacuum arc remelting (Ref. 10). In this process, a water-cooled copper crucible was charged with the desired composition for each compound. The charge consisted of the requisite combination of the granular elemental materials on a weight basis. The melting chamber was sealed, evacuated with a mechanical pump to a pressure of approximately  $10^{-3}$  torr, and then backfilled with argon to a partial pressure of approximately 500 torr ( $\sim 2/3$  atm). A tungsten electrode was used to strike an arc with the copper crucible, heating the charge to a molten state. To increase chemical homogeneity, each ingot was allowed to cool and then inverted in the crucible before being remelted. This process was repeated a total of five times, resulting in a small ingot weighing approximately 50g, as shown in Figure 1. The ingots were homogenized at 1050 °C for 48 in vacuum (approximately  $10^{-6}$  torr) followed by furnace cooling and then sectioned by wire electrical discharge machining into 5mm cubic specimens. The chemical compositions of the studied compounds (see Table 2) were analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES).

To study the effect of heat treatment temperature on microstructure and hardness, each specimen was heat treated for 2 hr at 800, 900 or 1,000 °C in vacuum. The binary compounds and the compounds containing 1 or 5 at.% Hf were also heat treated at 1,100 °C (also in vacuum). The furnace chamber was rapidly backfilled with argon so that the specimens could be drop-quenched in water. The heat treated specimens were mounted in Bakelite and prepared for microscopy with standard metallographic techniques, including a final polish using colloidal silica on a vibratory polisher. This procedure produced a high-quality surface finish for microscopic examination. It was discovered that the slight alkalinity of the colloidal silica solution used in the final polish provided a mild etch that enhanced the contrast between the medium grey parent B2 phase and the light grey  $\text{Ni}_3\text{Ti}$ , which forms as a large globular phase, and  $\text{Ni}_3\text{Ti}_2$  phases, which has a plate- or needle-like morphology (Refs. 11 and 12). It is important to note that the fine  $\text{Ni}_4\text{Ti}_3$  phase appears grey under examination by optical microscopy but it is, nevertheless, typically too fine to be resolved distinctly from the parent phase. Therefore, the second phase measurements included only the noncoherent  $\text{Ni}_3\text{Ti}$  and  $\text{Ni}_3\text{Ti}_2$  phases that reduce hardening.

TABLE 1.—CHEMICAL COMPOSITION OF ELEMENTAL MATERIALS  
USED IN THIS STUDY

Element	Purity, percent	Major impurities, ppm
Ni	99.999	C (10), Co (1), Fe (12) N (1), O (5), S (2)
Ti	99.995	C (11), Fe (5), H (1), N(<10), Ni (1), O (216), Rb (<5), S (<5), Sr (<3000), Ta (<5), Y (<200)
Ta	99.98	Nb (50), O (1200), H (<20), C (30), N (30), Si (<30), Ti (5), Mo (5), W (<10), Ni (<20), Fe (20), Cr (<10), Mn (5), Na (<10), K (<10), Nb (<30), Mg (5)
Hf	99.7	Al (<25), B (<0.5), Bi (<1), C (<20), Cd (<3), Cr (<30), Co (<5), Cu (<20), Fe (<50), H (<3), Mg (<10), N (<5), Nb (<50), Ni (<25), O (<53), P (<3), Pb (<5), S (<10), Si (<25), Sn (<10), Ta (<1), Th (<4), Ti (<20), U (<2), V (<10), W (<20), Zr (14000)
Zr	99.5	Al (<20), B (<0.25), C (<31), Cd (<0.25), Co (<10), Cr (<50), Cu (<25), Fe (<50), H (22), Hf (28), Mn (<25), Mo (<10), N (<20), Nb (<50), Ni (<35), O (80), P (5), Pb (<25), Si (<10), Sn (<35), Ta (<100), Ti (<25), U (<1), V (<25), W (<30)

TABLE 2.—COMPOSITIONS OF THE STUDIED INTERMETALLIC COMPOUNDS

Designation	Target composition, at. %	Ni, wt. % [at. %]	Ti, wt. % [at. %]	X, wt. % [at. %]	Impurities, ppm
51	Ni <sub>51</sub> -Ti <sub>49</sub>	56.2 [51.1]	43.8 [48.9]	N/A	Al (30), B (40), Ca (1), Fe (10), Mn (2), Mo (20), Si (40), C (120), N (15), O (230)
52	Ni <sub>52</sub> -Ti <sub>48</sub>	56.8 [51.8]	43.1 [48.2]	N/A	Al (10), Cu (40), Fe (10), Mo (30), C (80), N (<10), O (160)
53	Ni <sub>53</sub> -Ti <sub>47</sub>	57.7 [52.7]	42.2 [47.3]	N/A	Al (50), Cu (90), Fe (30), Mo (30), C (115), N (25), O (325)
54	Ni <sub>54</sub> -Ti <sub>46</sub>	58.3 [53.6]	41.1 [46.3]	N/A	Al (10), Cu (20), Fe (20), Mo (30), W (4800), C (80), N (10), O (230)
55	Ni <sub>55</sub> -Ti <sub>45</sub>	59.1 [54.2]	40.7 [45.8]	N/A	Al (10), Co (20), Cu (100), Fe (10), Mo (30), W (1300), C (80), N (<10), O (220)
56	Ni <sub>56</sub> -Ti <sub>44</sub>	60.4 [55.5]	39.5 [44.5]	N/A	Al (10), Co (20), Cu (80), Fe (20), Mo (30), W (200), C (75), N (10), O (210)
52-1H	Ni <sub>52</sub> -Ti <sub>47</sub> -Hf <sub>1</sub>	55.4 [51.7]	41.3 [47.3]	3.25 Hf [1.00]	Al (20), Cu (60), Fe (20), Mo (20), Zr (400), C (60), N (35), O (205)
53-1H	Ni <sub>53</sub> -Ti <sub>46</sub> -Hf <sub>1</sub>	56.8 [53.1]	40.0 [45.9]	3.15 Hf [0.97]	Al (20), Cu (70), Fe (10), Mo (20), Zr (400), C (60), N (<10), O (180)
54-1H	Ni <sub>54</sub> -Ti <sub>45</sub> -Hf <sub>1</sub>	57.6 [54.4]	38.4 [44.4]	3.27 Hf [1.01]	Al (20), Co (40), Cu (700), Fe (10), Mo (20), W (5300), Zr (400), C (70), N (10), O (260)
55-1H	Ni <sub>55</sub> -Ti <sub>44</sub> -Hf <sub>1</sub>	56.9 [53.3]	39.8 [45.7]	3.16 Hf [0.97]	Al (10), Cu (20), Fe (10), Mo (20), W (50), Zr (400), C (70), N (30), O (280)
52-3H	Ni <sub>52</sub> -Ti <sub>45</sub> -Hf <sub>3</sub>	53.3 [52.5]	36.7 [44.3]	9.73 Hf [3.15]	Zr (1300), Cu (250), Fe (15), Mn (3), Mo (20), Si (140), C (70), N (3), O (410)
53-3H	Ni <sub>53</sub> -Ti <sub>44</sub> -Hf <sub>3</sub>	54.4 [53.6]	35.9 [43.3]	9.46 Hf [3.06]	Zr (1300), Cu (330), Fe (15), Mn (3), Mo (20), Si (140), C (60), N (3), O (330)
54-3H	Ni <sub>54</sub> -Ti <sub>43</sub> -Hf <sub>3</sub>	55.2 [54.6]	34.9 [42.3]	9.48 Hf [3.08]	Zr (1300), Cu (310), Fe (15), Mn (6), Mo

Designation	Target composition, at.%	Ni, wt.% [at.%]	Ti, wt.% [at.%]	X, wt.% [at.%]	Impurities, ppm
					(20), Si (980), C (60), N (2), O (310)
55-3H	Ni <sub>55</sub> -Ti <sub>42</sub> -Hf <sub>3</sub>	56.0 [55.4]	34.1 [41.4]	9.61 Hf [3.13]	Zr (1300), Cu (50), Fe (15), Mn (6), Mo (20), Si (80), C (60), N (2), O (180)
52-3T	Ni <sub>52</sub> -Ti <sub>45</sub> -Hf <sub>3</sub>	53.5 [52.7]	36.6 [44.2]	9.71 Ta [3.10]	Cu (400), Fe (35), Mn (4), Mo (20), Si (160), C (70), N (6), O (400)
53-3T	Ni <sub>53</sub> -Ti <sub>44</sub> -Hf <sub>3</sub>	54.5 [53.7]	35.8 [43.2]	9.63 Ta [3.08]	Cu (290), Fe (35), Mn (5), Mo (20), Si (160), C (70), N (3), O (370)
54-3T	Ni <sub>54</sub> -Ti <sub>43</sub> -Hf <sub>3</sub>	55.2 [54.5]	35.0 [42.4]	9.68 Ta [3.10]	Cu (80), Fe (35), Mn (7), Mo (20), Si (400), C (60), N (1), O (200)
55-3T	Ni <sub>55</sub> -Ti <sub>42</sub> -Hf <sub>3</sub>	56.0 [55.5]	34.2 [41.4]	9.66 Ta [3.10]	Cu (10), Fe (35), Mn (8), Mo (20), Si (700), C (60), N (2), O (220)
52-3Z	Ni <sub>52</sub> -Ti <sub>45</sub> -Zr <sub>3</sub>	56.2 [52.6]	38.5 [44.2]	5.22 Zr [3.15]	Cu (130), Fe (10), Mn (3), Mo (20), Si (200), C (70), N (210), O (340)
53-3Z	Ni <sub>53</sub> -Ti <sub>44</sub> -Zr <sub>3</sub>	57.1 [53.6]	37.6 [43.3]	5.17 Zr [3.12]	Cu (40), Fe (10), Mn (5), Mo (20), Si (190), C (70), N (2), O (240)
54-3Z	Ni <sub>54</sub> -Ti <sub>43</sub> -Zr <sub>3</sub>	57.8 [54.4]	36.7 [42.4]	5.25 Zr [3.18]	Cu (80), Fe (10), Mn (8), Mo (20), Si (800), C (60), N (10), O (260)
55-3Z	Ni <sub>55</sub> -Ti <sub>42</sub> -Zr <sub>3</sub>	58.9 [55.5]	35.7 [41.3]	5.26 Zr [3.19]	Cu (<10), Fe (15), Mn (2), Mo (20), Si (670), C (60), N (2), O (200)
52-5H	Ni <sub>52</sub> -Ti <sub>43</sub> -Hf <sub>5</sub>	50.8 [52.1]	34.0 [42.8]	14.9 Hf [5.02]	Al (30), Cu (20), Fe (10), Mo (20), Zr (2000), C (60), N (<10), O (150)
53-5H	Ni <sub>53</sub> -Ti <sub>42</sub> -Hf <sub>5</sub>	51.0 [52.4]	33.8 [42.5]	14.9 Hf [5.03]	Al (20), Cu (40), Fe (30), Mo (20), Zr (2100), C (75), N (25), O (235)
54-5H	Ni <sub>54</sub> -Ti <sub>41</sub> -Hf <sub>5</sub>	52.6 [54.1]	32.3 [40.8]	14.8 Hf [5.00]	Al (20), Cu (20), Fe (20), Mo (20), Zr (2100), C (60), N (<10), O (140)
55-5H	Ni <sub>55</sub> -Ti <sub>40</sub> -Hf <sub>5</sub>	53.5 [55.0]	31.6 [39.9]	14.6 Hf [4.95]	Al (10), Co (20), Cu (90), Fe (10), Mo (20), W (100), Zr (2100), C (74), N (24), O (240)

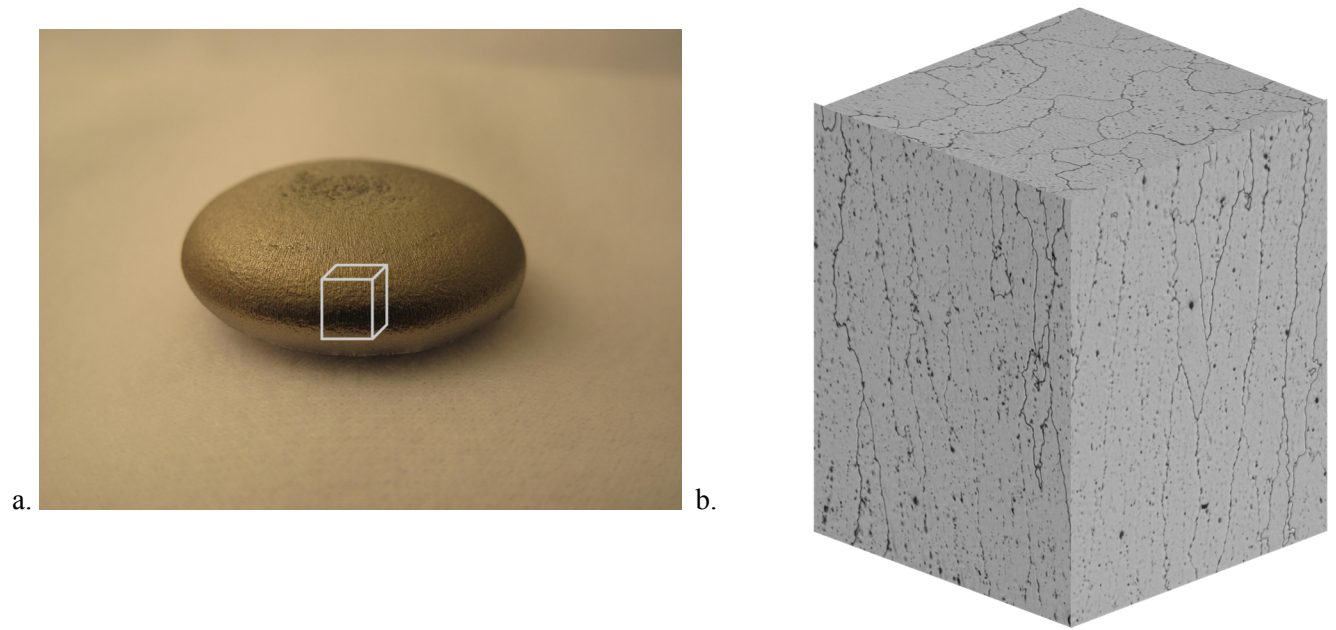


Figure 1.—(a) Example of a Ni-Ti ingot fabricated by vacuum arc remelting and (b) representative microstructure of the material in the orientations indicated by the cube in (a). The orientation of the grains, which tends to be orthogonal to the bottom of the crucible, obeys the customary solidification kinetics, aligning in the direction of heat removal.

Commercially available image analysis software was used to calculate the percentage of second phase present in each compound. A total area of approximately  $9 \times 10^5 \mu\text{m}^2$  was analyzed for each specimen. The image analysis was performed at a magnification of  $200\times$  and the software measurement system was calibrated such that each pixel corresponded to approximately  $0.5 \mu\text{m}$  both vertically and horizontally. Each monochromatic photomicrograph had a bit-depth of 8 bits per pixel with an image resolution of 1,360 by 1,024 pixels. Thresholding was selected between 170 (grey) and 255 (black) so that the secondary phase was distinct from the parent phase. A typical example of a microstructure and the accompanying analyzed image is shown in Figure 2. Due to the very consistent grey level of the parent phase, it was possible to compute its coverage area, excluding the lighter shades of grey comprising the secondary phases. Please note that, in this document, all phases other than parent phase NiTi are classified with the general term “secondary phases.” These primarily consisted of  $\text{Ni}_3\text{Ti}$ , possibly small amounts of  $\text{Ni}_3\text{Ti}_2$ , and very small quantities of oxides and carbides, based upon previous studies (Refs. 11 and 12). Detailed phase identification for the compounds studied in this investigation will be provided in future publications.

Vickers microindentation hardness was measured using standard procedures (Ref. 13). Unlike the standard method, however, a linear indentation spacing of  $500 \mu\text{m}$  was used to eliminate any near-field strain-hardening, which was found to be an issue with this material. Care was taken to avoid making indentations on clusters of precipitate phase material as this tended to distort the edges of the indentations. The average of five hardness measurements at every heat treatment condition is reported for each alloy.

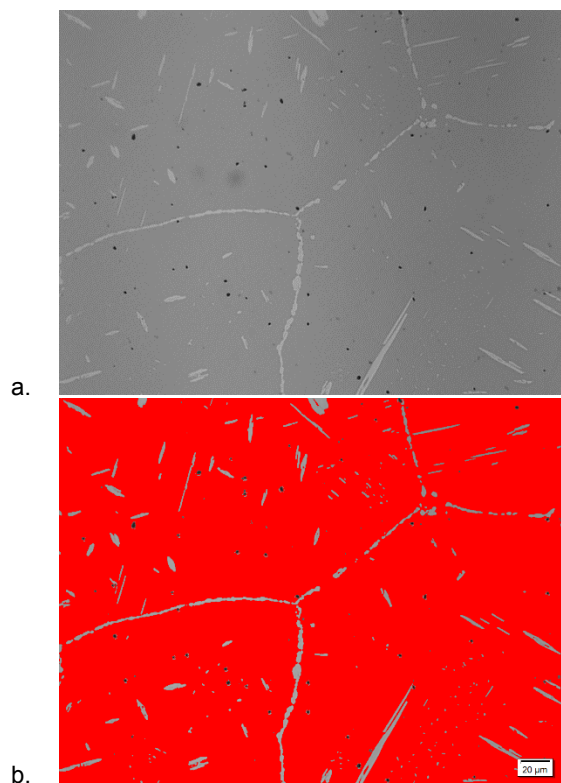


Figure 2.—(a) Optical micrograph and (b) corresponding image after conversion for image analysis showing the parent phase in red and the precipitate phases in grey. The specimen is alloy 55-1H (55 at.% Ni – 44 at.% Ti – 1 at.% Hf) after heat treatment at  $900^\circ\text{C}$  for 2 h (water quench) and the second phase comprises approximately 4 percent of the image.

## Results

### Microstructures

Optical micrographs of each of the studied compounds are shown in Figures 3 through 30.

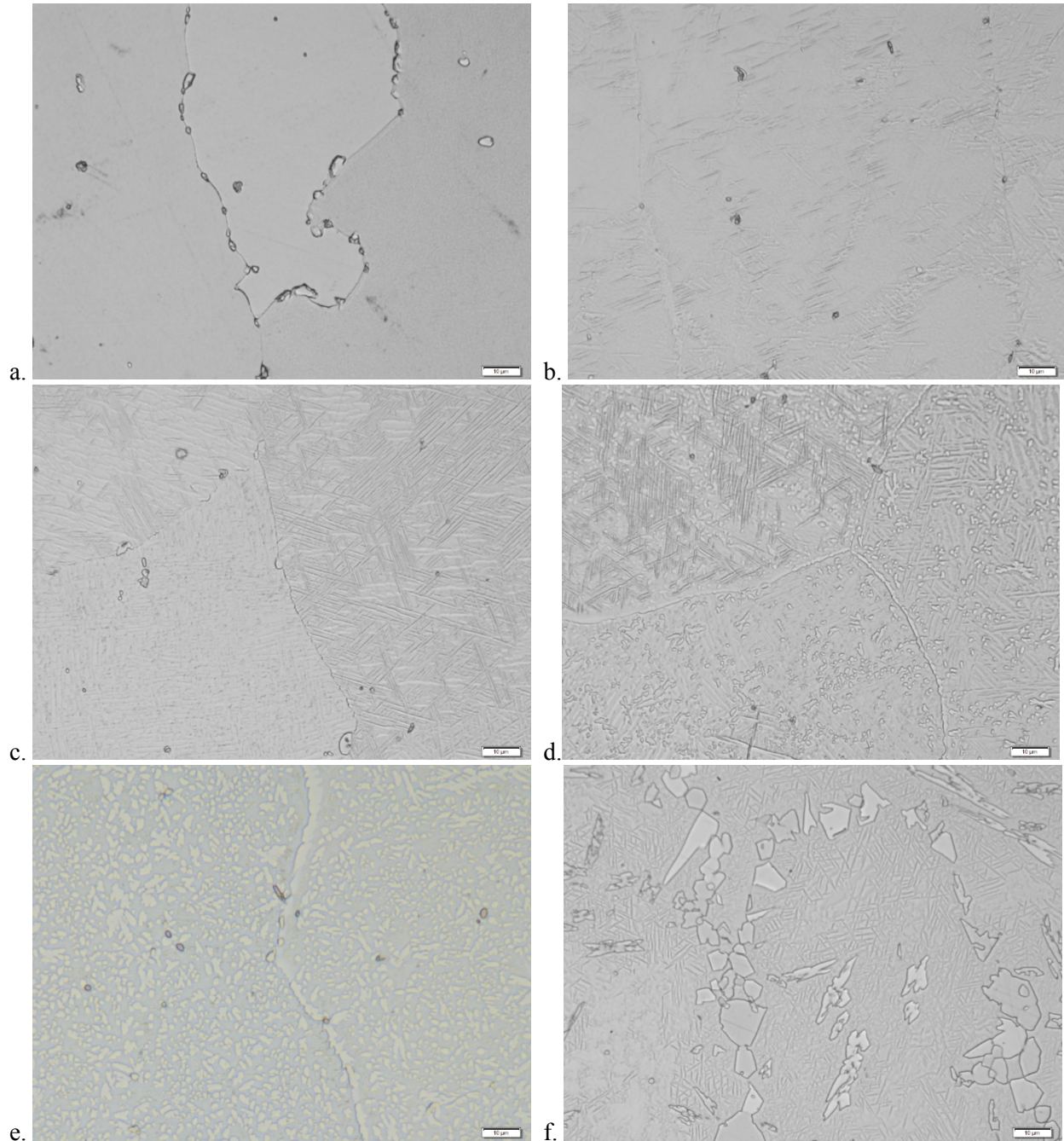


Figure 3.—Brightfield optical photomicrographs showing alloys (a) 51, (b) 52, (c) 53, (d) 54, (e) 55, and (f) 56 after homogenization at 1,050 °C for 48 hr followed by furnace cooling. The homogenized microstructure represents an equilibrium microstructure. Work is underway to identify the fine phases.



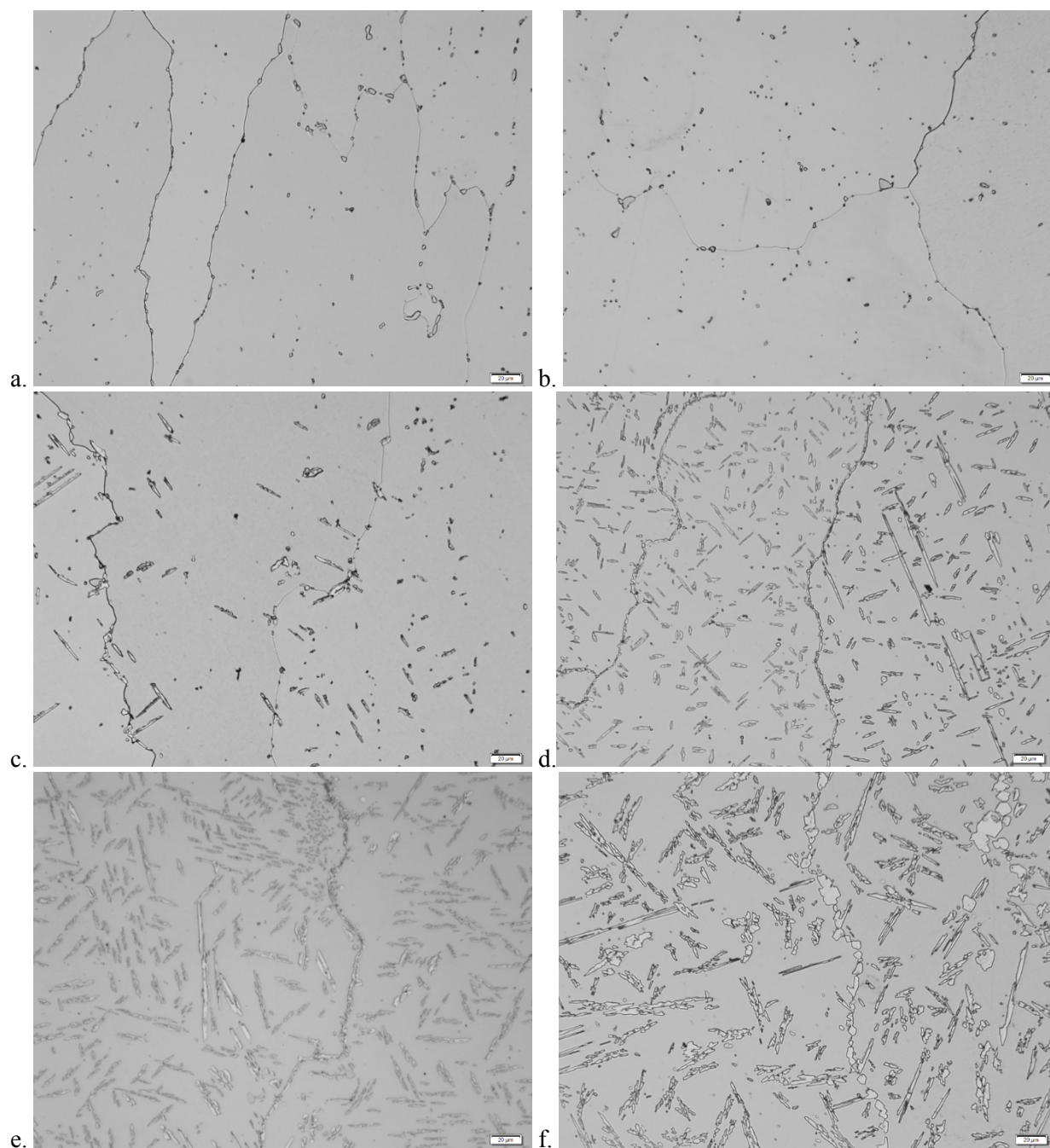


Figure 4.—Brightfield optical photomicrographs showing alloys (a) 51, (b) 52, (c) 53, (d) 54, (e) 55, and (f) 56 after heat treatment at 800 °C for 2 hr (water quench). The photomicrographs show the increase of second phase with increasing Ni content from (a) to (f).



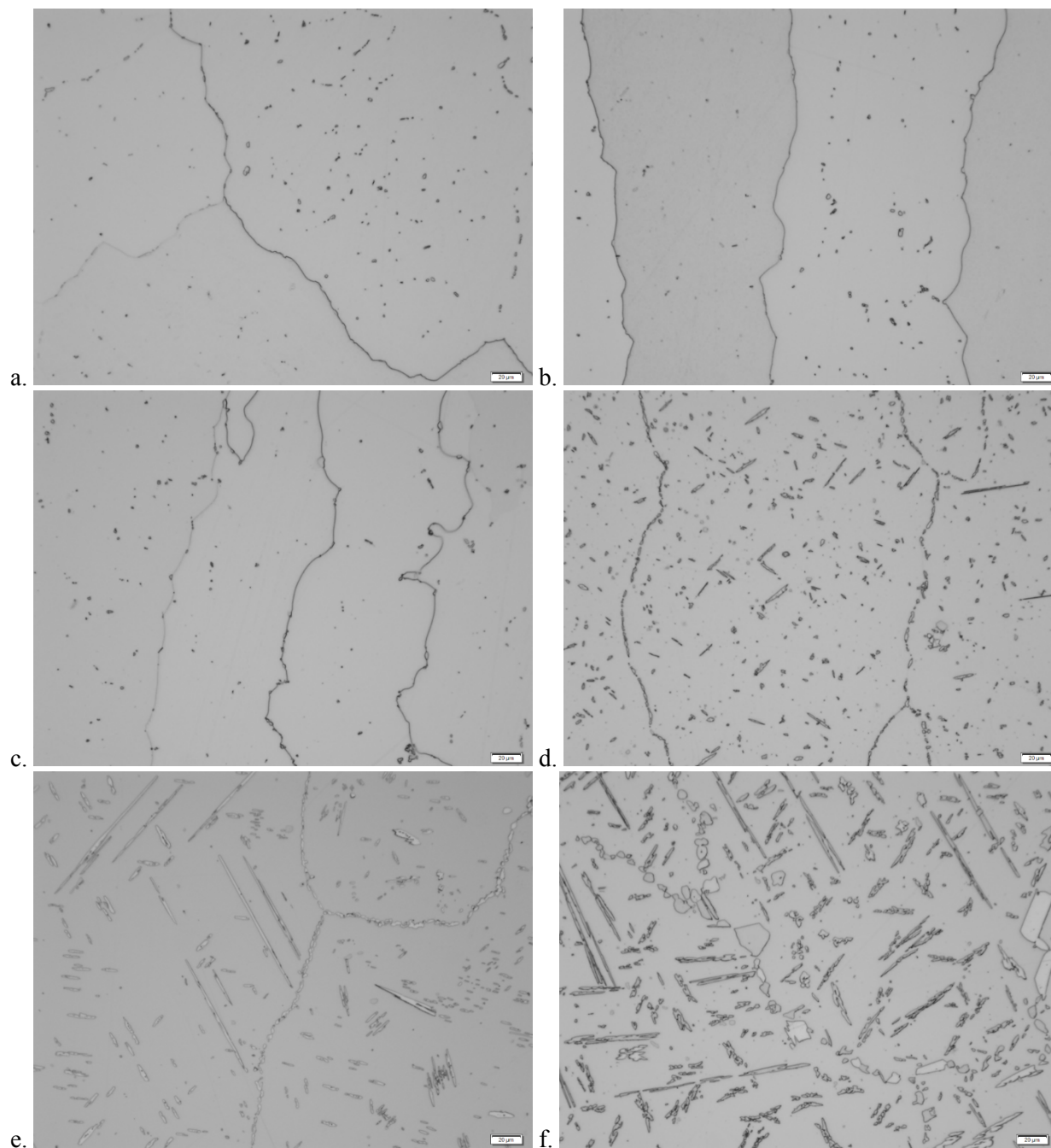


Figure 5.—Brightfield optical photomicrographs showing alloys (a) 51, (b) 52, (c) 53, (d) 54, (e) 55, and (f) 56 after heat treatment at 900 °C for 2 hr (water quench). The photomicrographs show the increase of second phase with increasing Ni content from a to f.

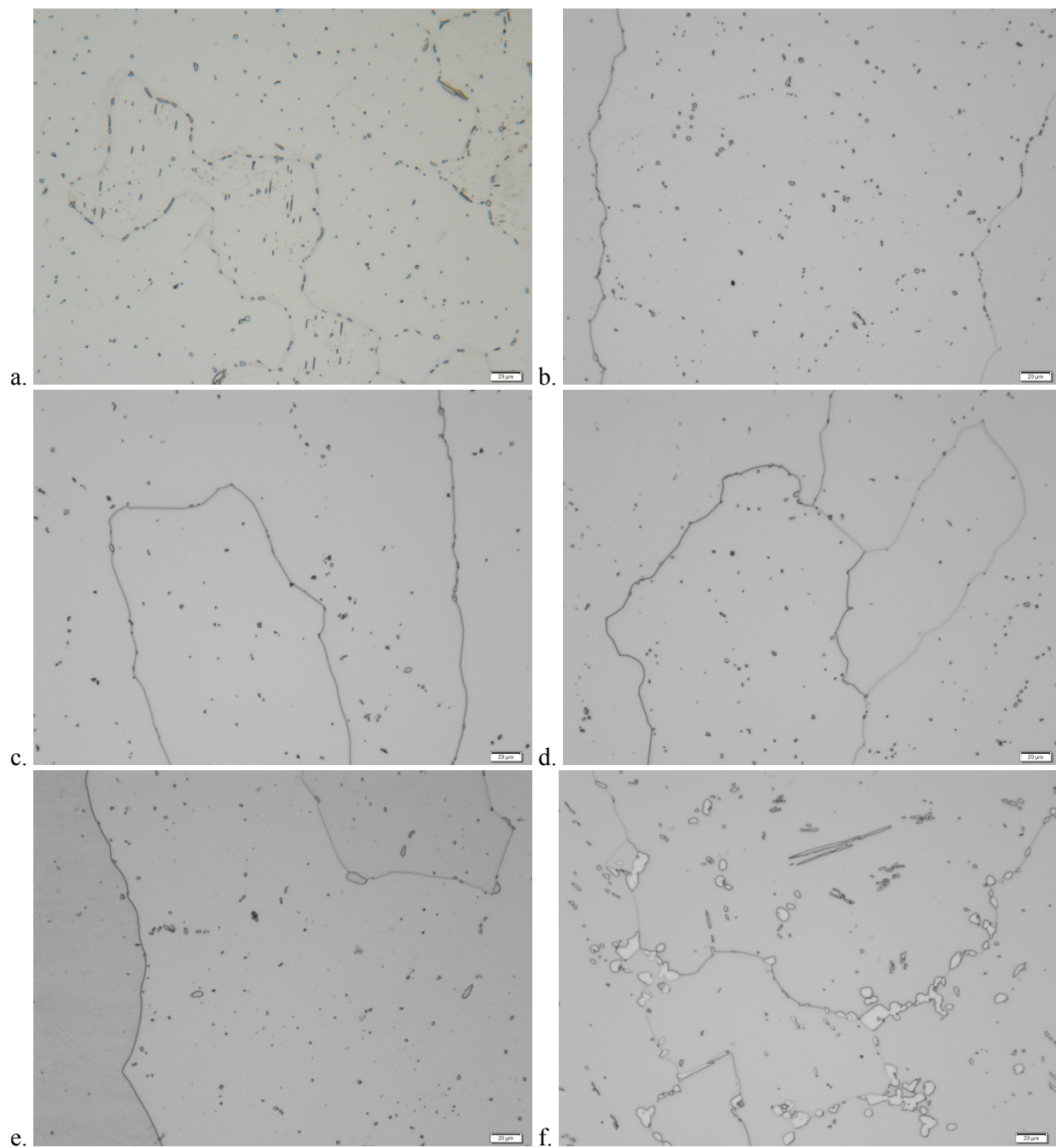


Figure 6.—Brightfield optical photomicrographs showing alloys (a) 51, (b) 52, (c) 53, (d) 54, (e) 55, and (f) 56 after heat treatment at 1,000 °C for 2 hr (water quench). At this temperature, the only compound to generate precipitates was alloy 56 (e).

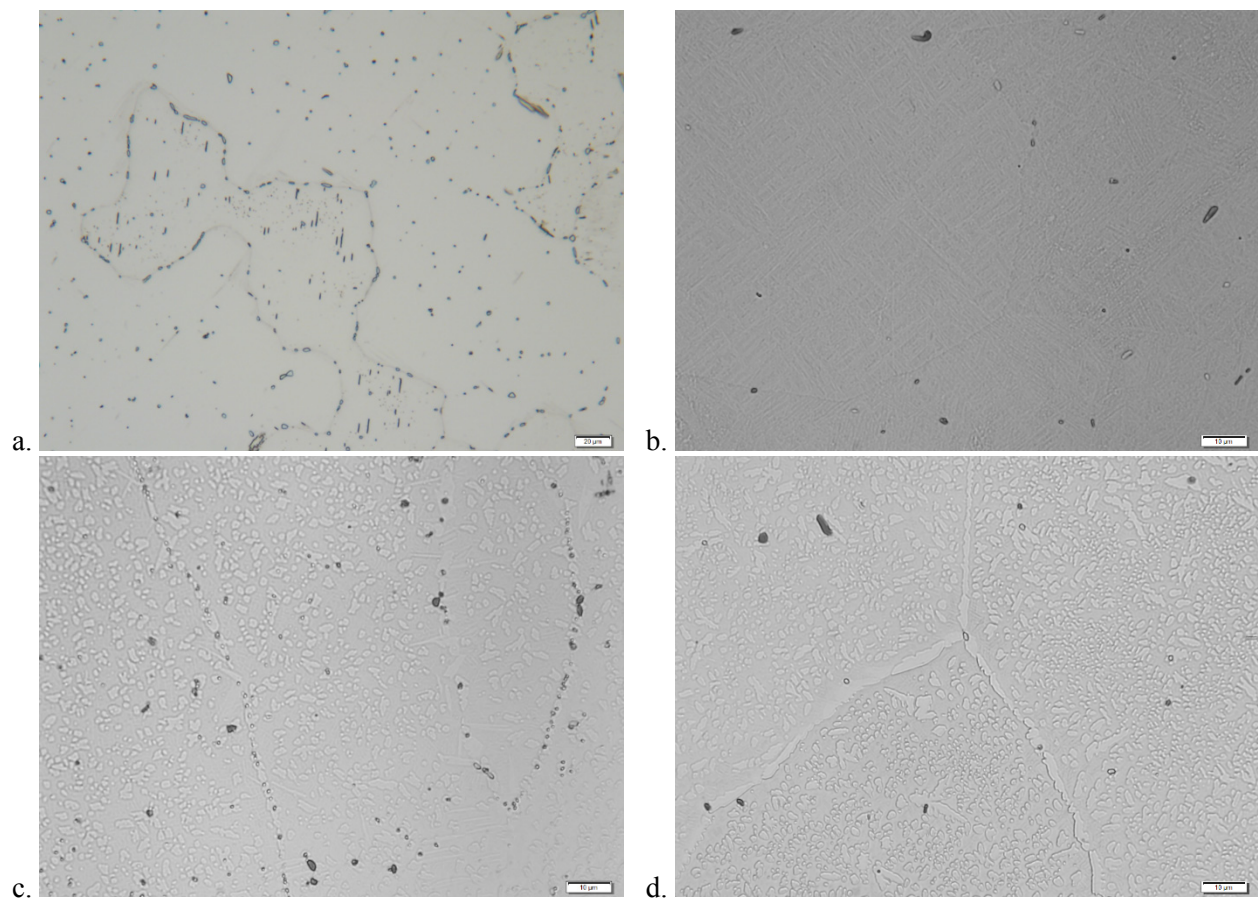


Figure 7.—Optical micrographs of alloys (a) 52-1H, (b) 53-1H, (c) 54-1H, and (d) 55-1H after vacuum homogenization at 1,050 °C and furnace cooling.

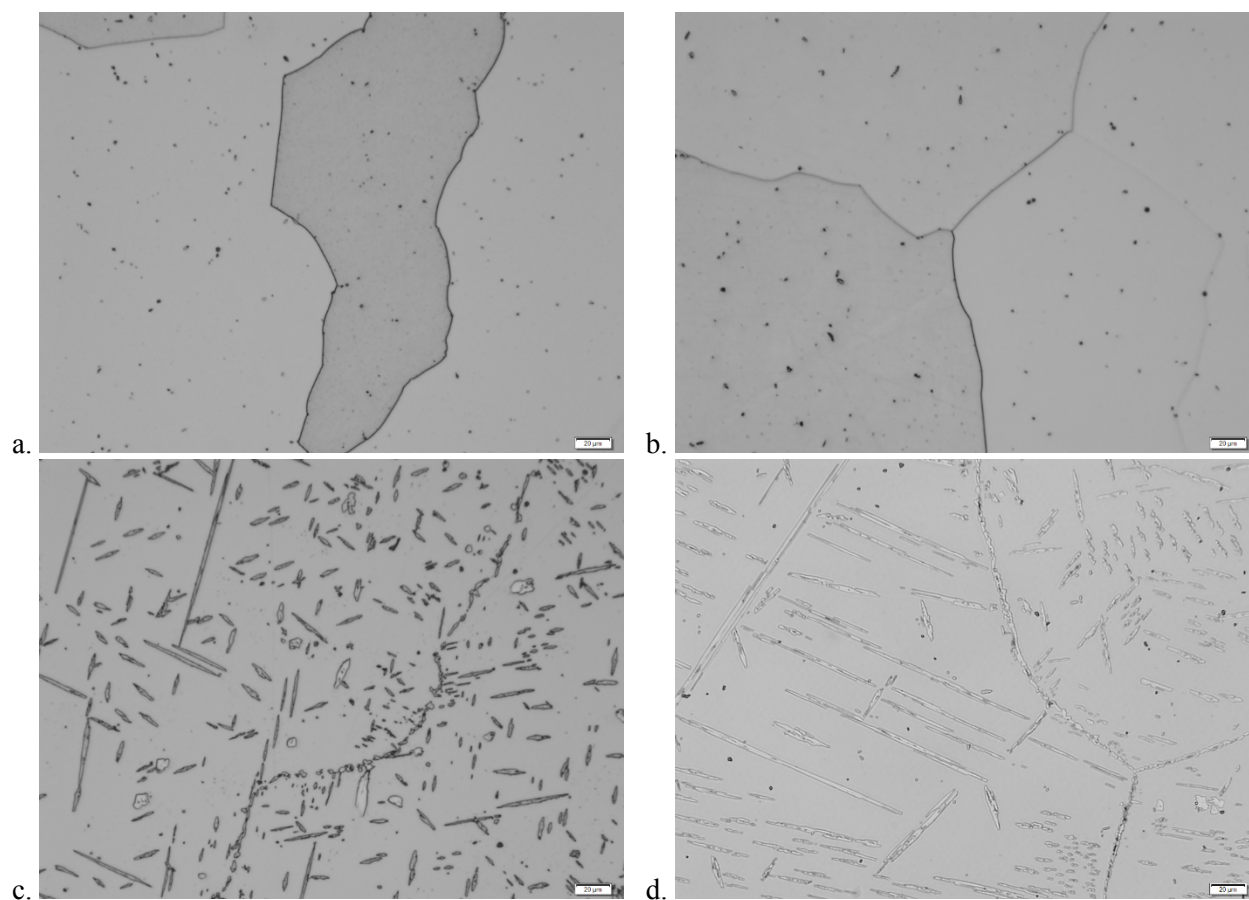


Figure 8.—Optical micrographs of alloys (a) 52-1H, (b) 53-1H, (c) 54-1H, and (d) 55-1H after heat treatment at 800 °C. These photomicrographs show the increase of second phase with increasing Ni content.

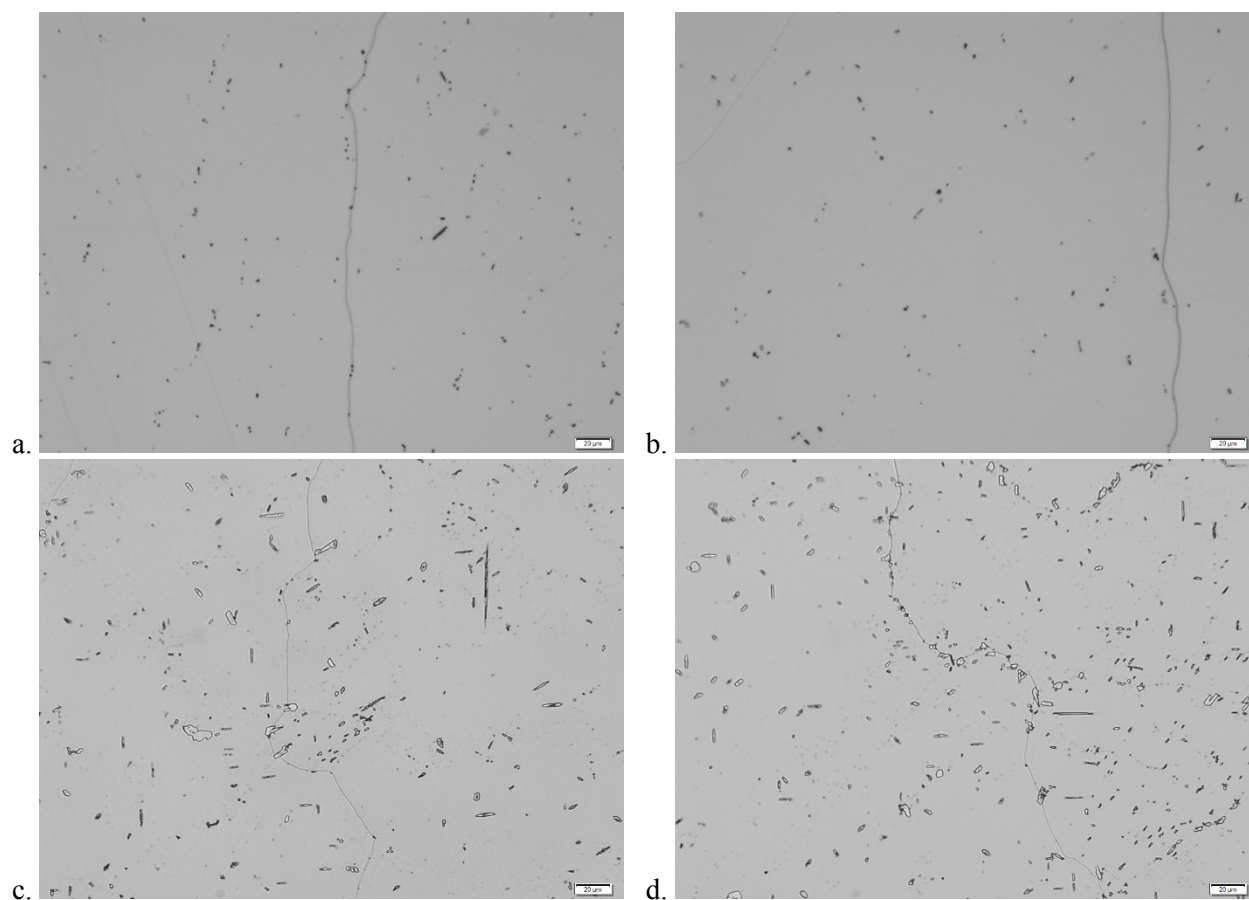


Figure 9.—Optical micrographs of alloys (a) 52-1H, (b) 53-1H, (c) 54-1H, and (d) 55-1H after heat treatment at 900 °C. These photomicrographs show very little increase in second phase with increasing Ni content.



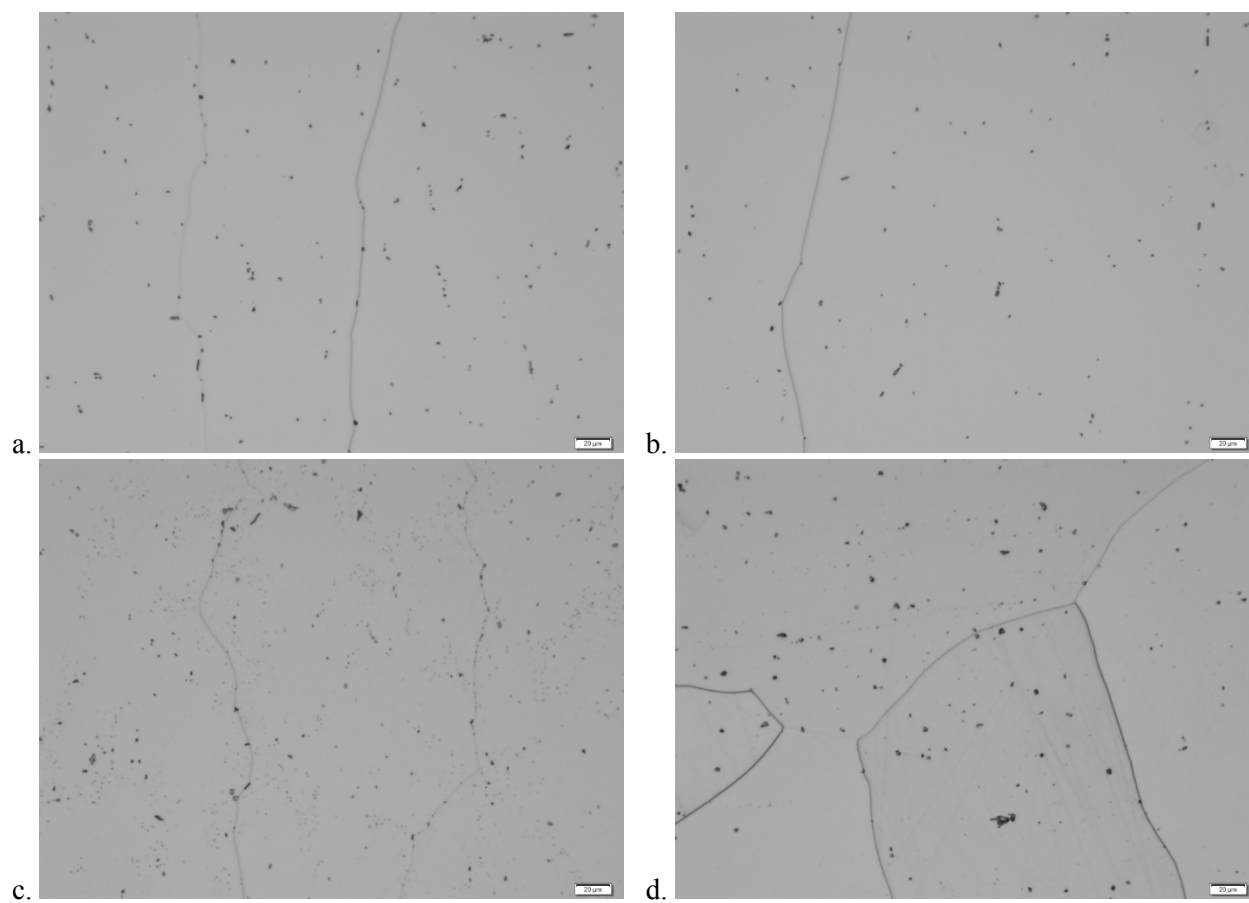


Figure 10.—Optical micrographs of alloys (a) 52-1H, (b) 53-1H, (c) 54-1H, and (d) 55-1H after heat treatment at 1,000 °C. These photomicrographs show that little, if any, precipitation product is formed during this heat treatment.

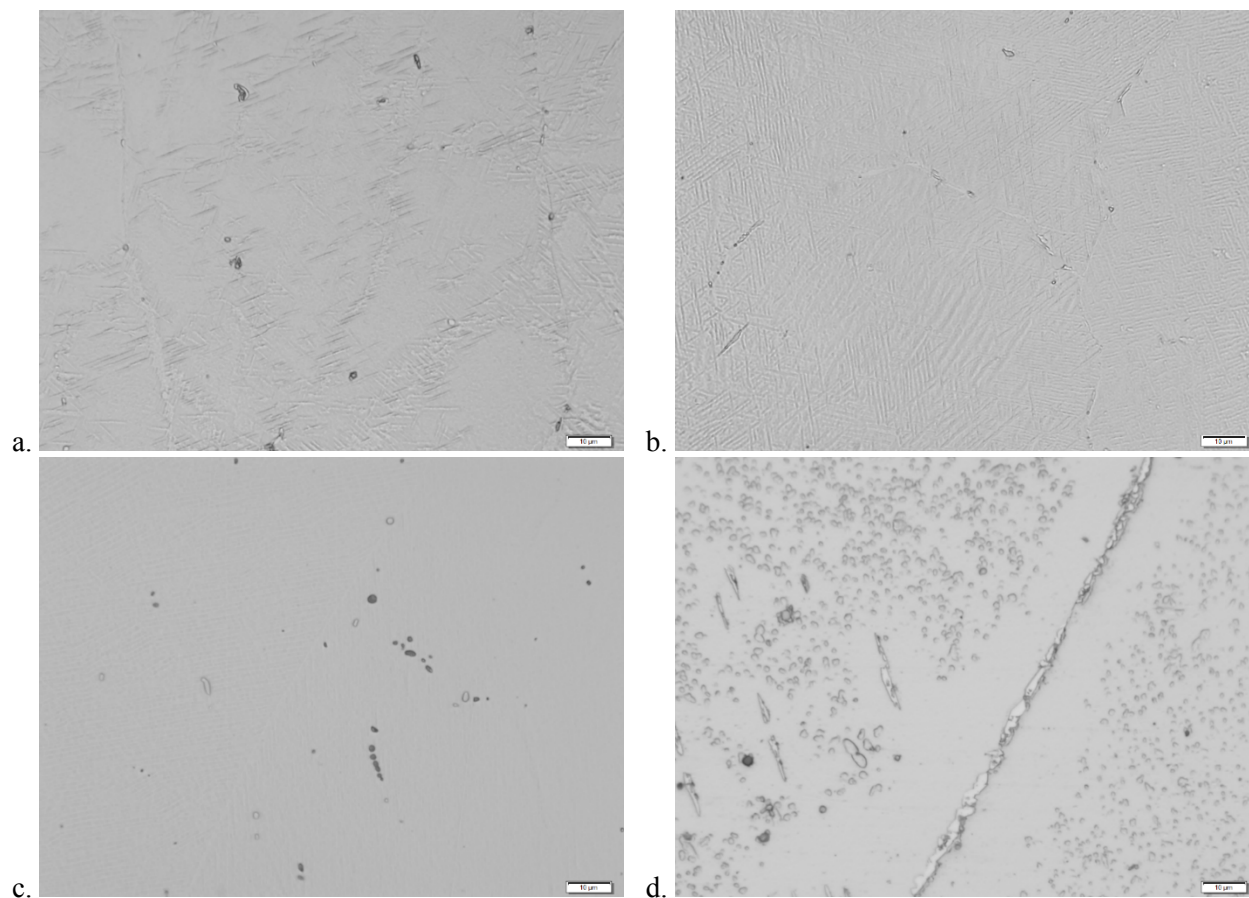


Figure 11.—Photomicrographs showing alloys (a) 52, (b) 52-3T, (c) 52-3H, and (d) 52-3Z after vacuum homogenization at 1,050 °C and furnace cooling.

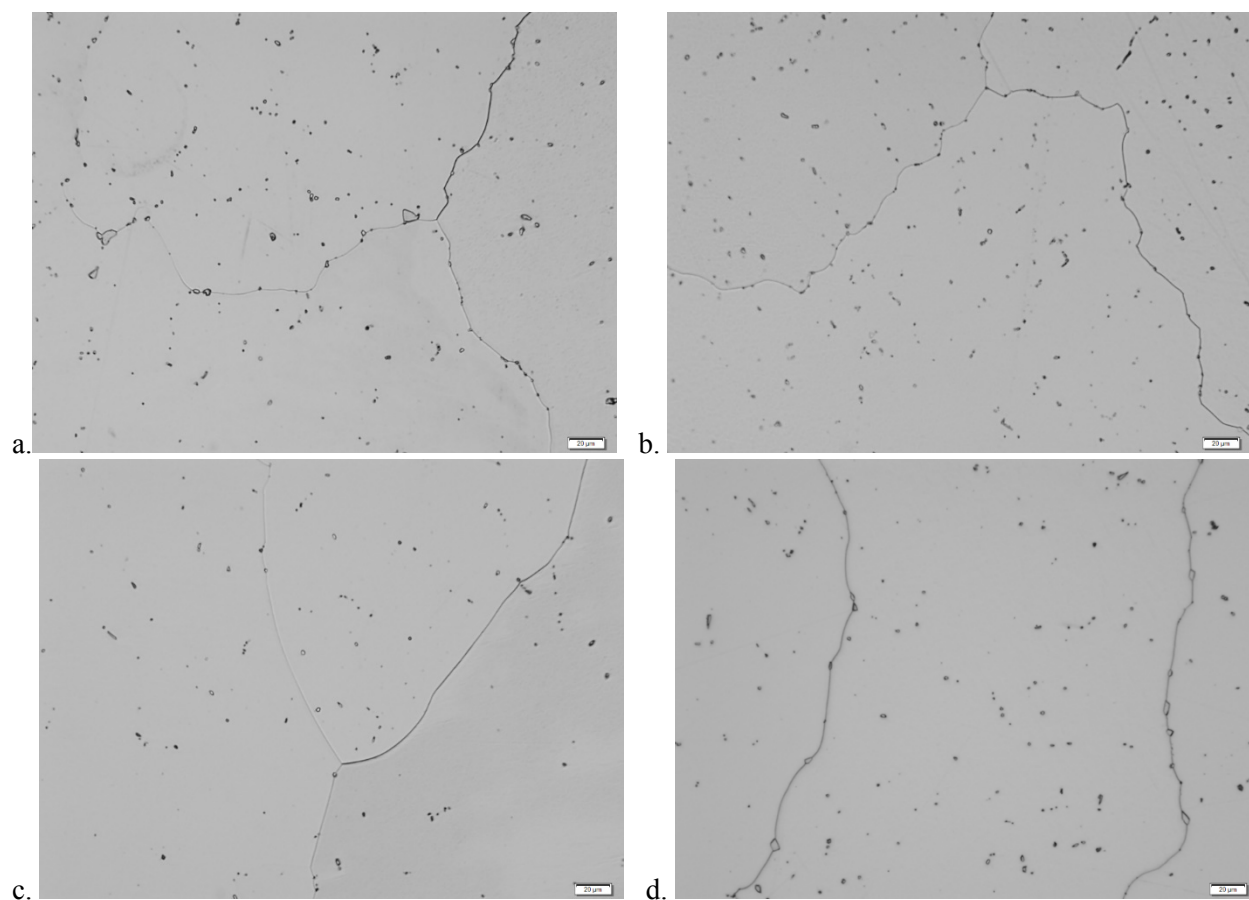


Figure 12.—Photomicrographs showing alloys (a) 52, (b) 52-3T, (c) 52-3H, and (d) 52-3Z after heat treatment at 800 °C. These photomicrographs show that little, if any, precipitation product is formed during this heat treatment.



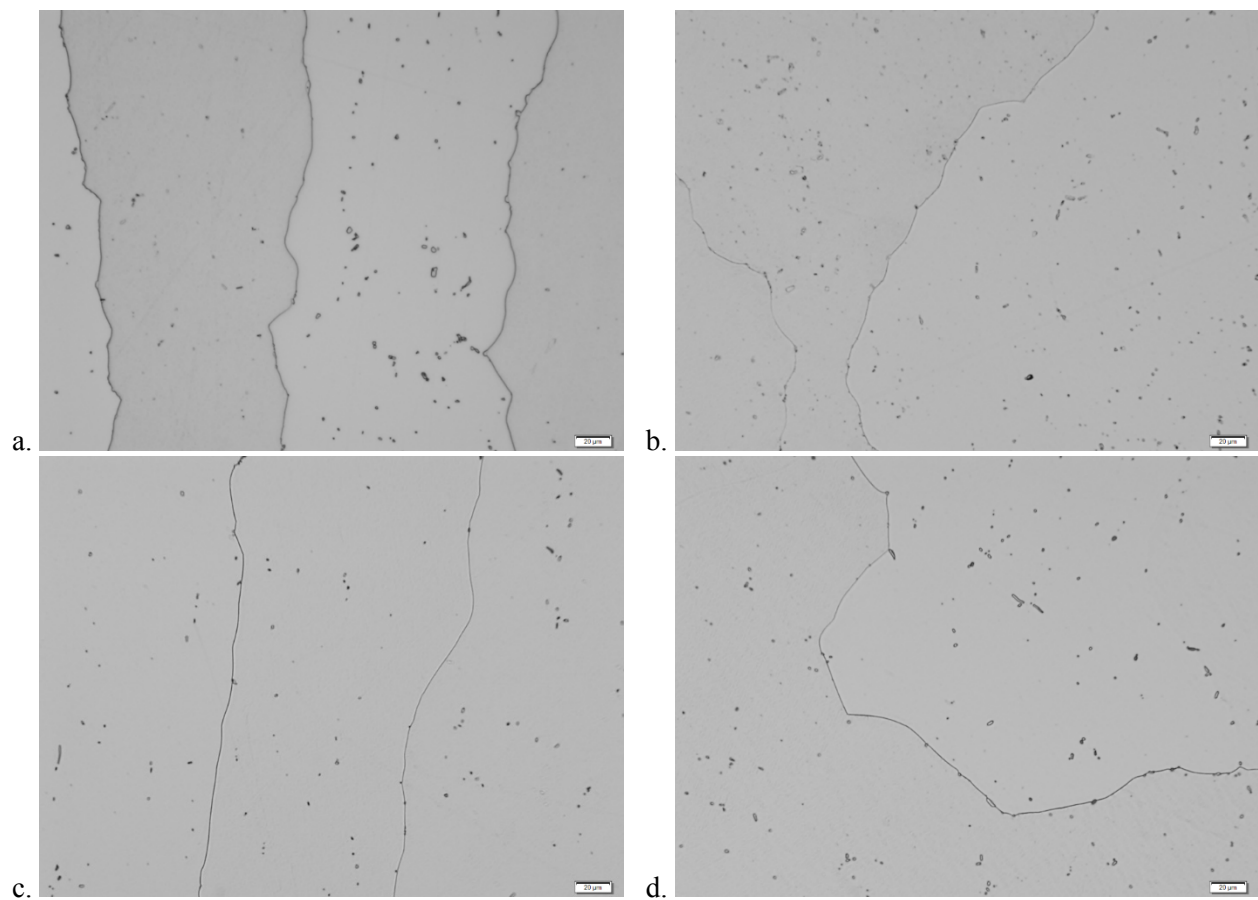


Figure 13.—Photomicrographs showing alloys (a) 52, (b) 52-3T, (c) 52-3H, and (d) 52-3Z after heat treatment at 900 °C. These photomicrographs show that little, if any, precipitation product is formed during this heat treatment.

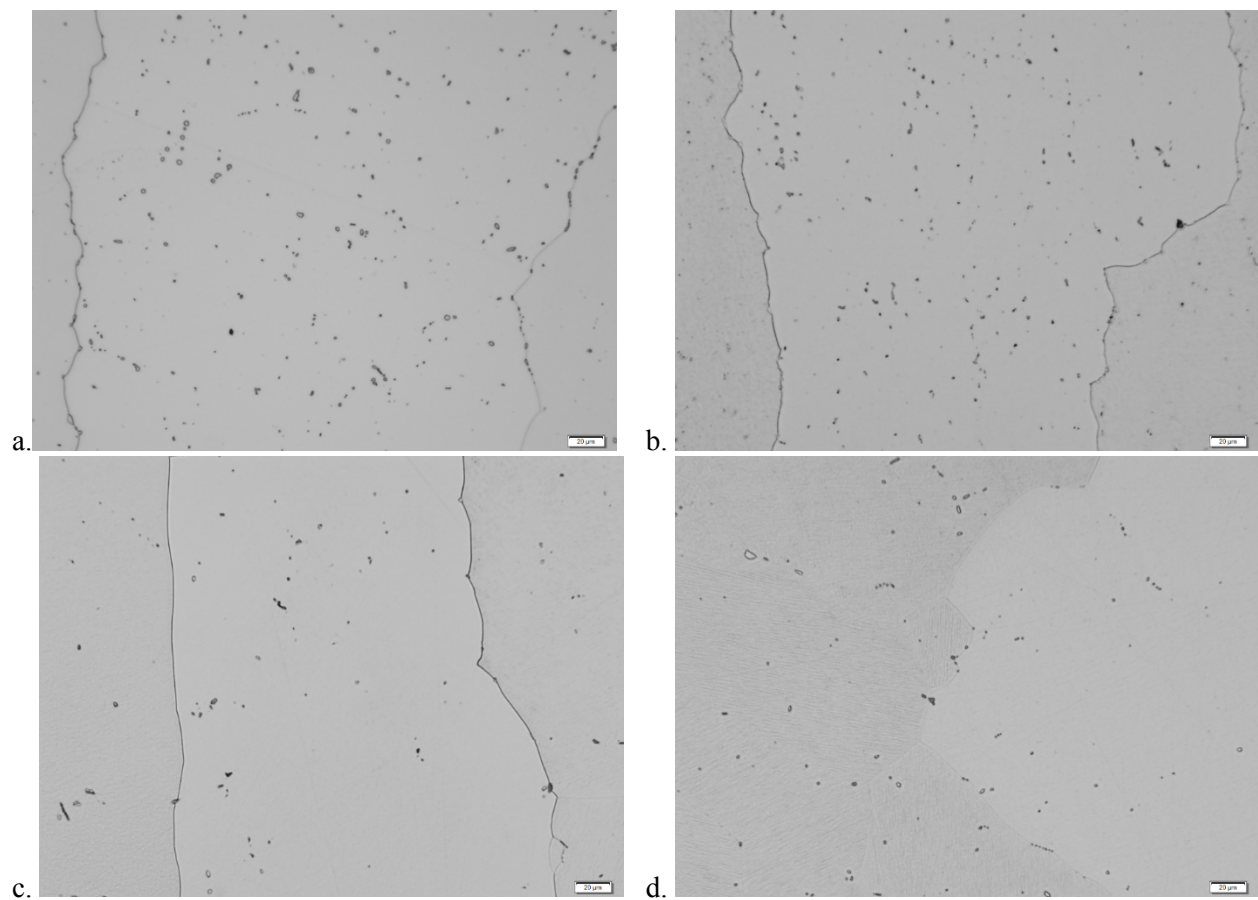


Figure 14.—Photomicrographs showing alloys (a) 52, (b) 52-3T, (c) 52-3H, and (d) 52-3Z after heat treatment at 1,000 °C. These photomicrographs show that little, if any, precipitation product is formed during this heat treatment.

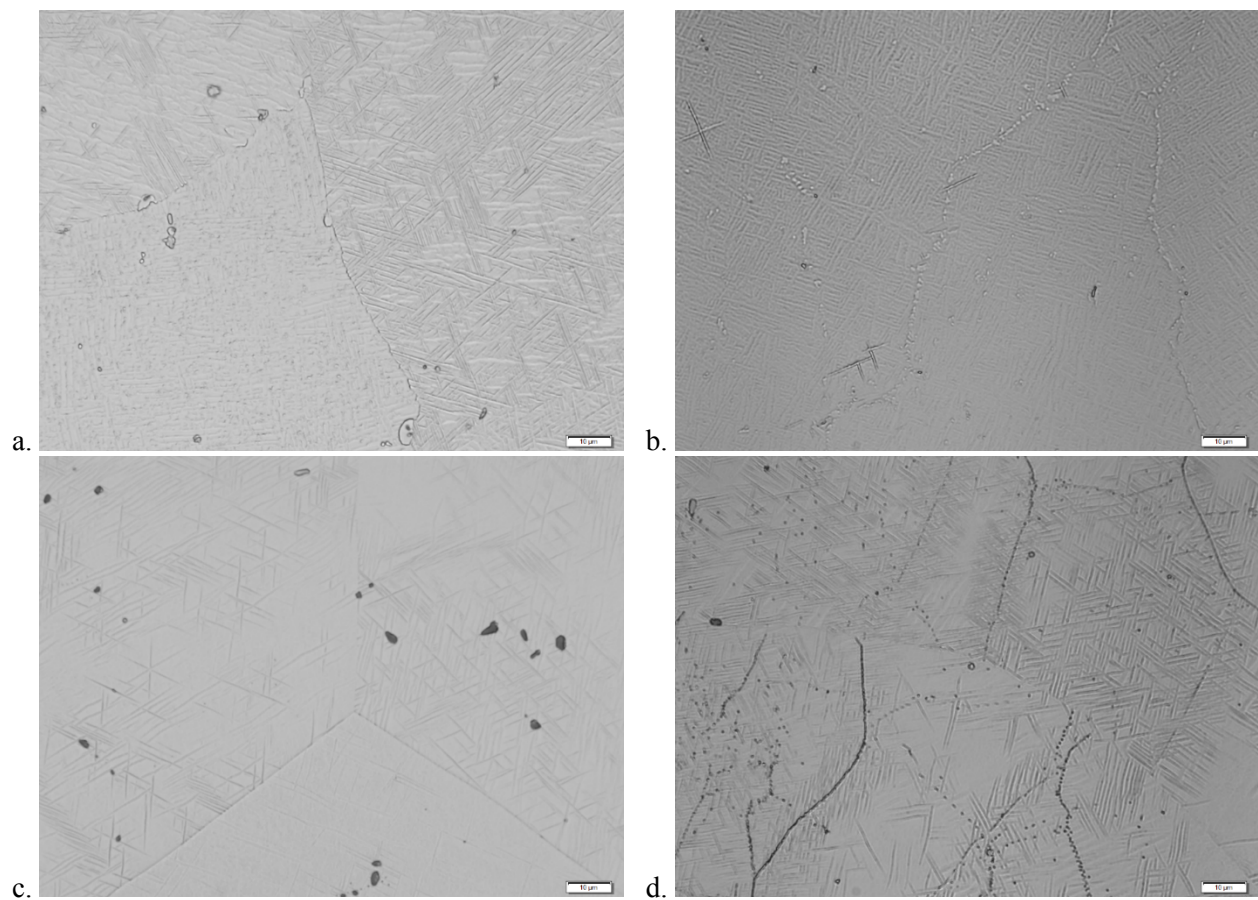


Figure 15.—Photomicrographs showing alloys (a) 53, (b) 53-3T, (c) 53-3H, and (d) 53-3Z after homogenization at 1,050 °C for 48 hr and furnace cooling.

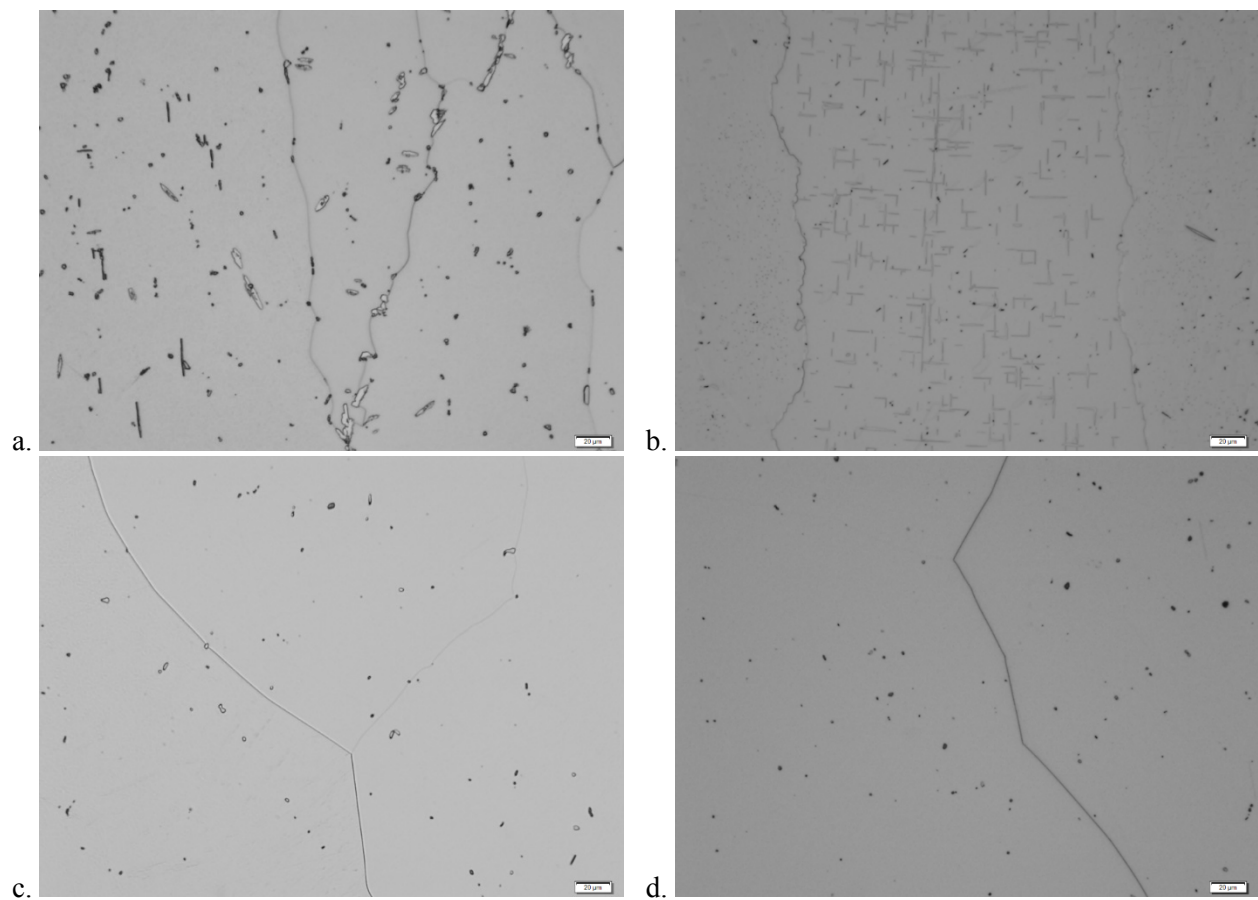


Figure 16.—Photomicrographs showing alloys (a) 53, (b) 53-3T, (c) 53-3H, and (d) 53-3Z after heat treatment at 800 °C. Little, if any, precipitation product is present in alloys 53-3H and 53-3Z (c-d).

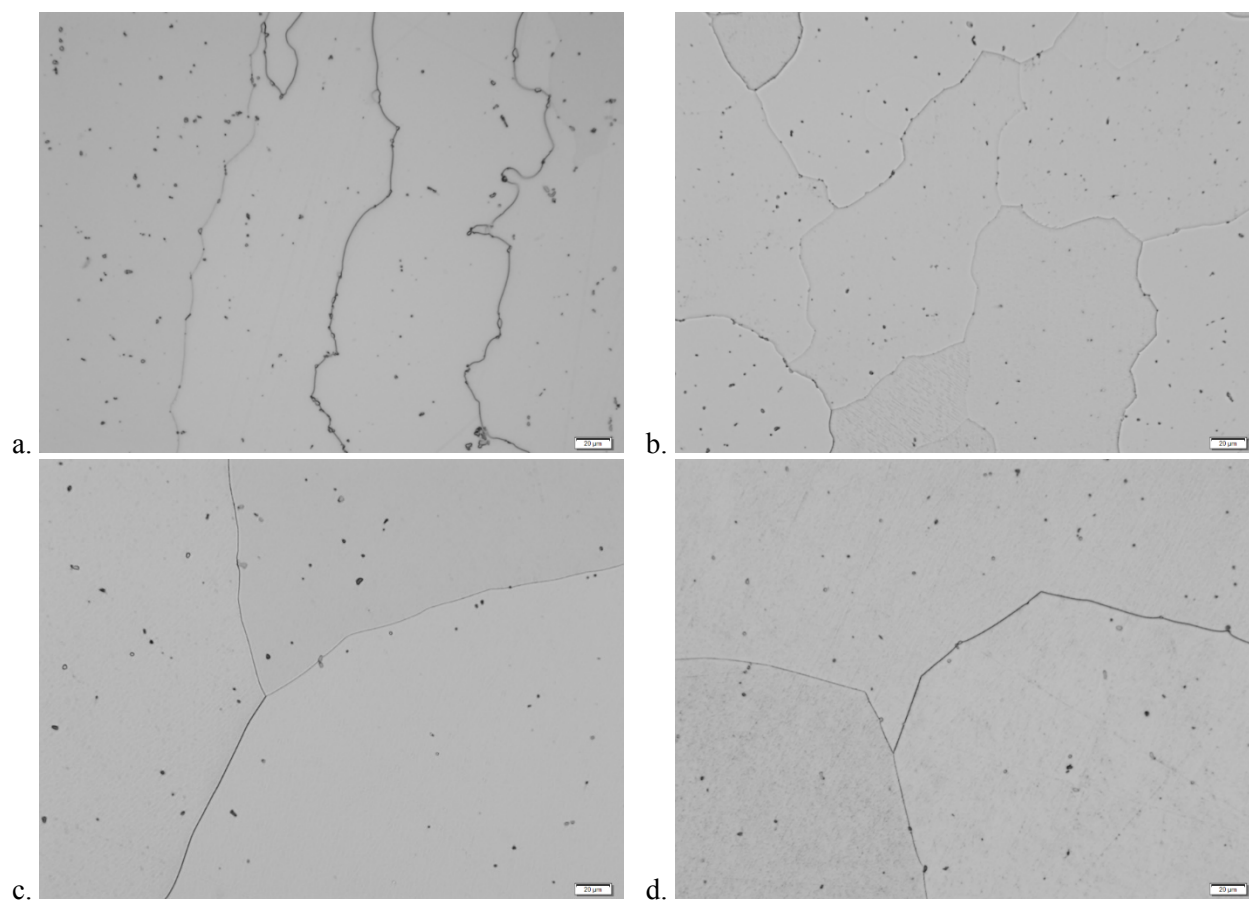


Figure 17.—Photomicrographs showing alloys (a) 53, (b) 53-3T, (c) 53-3H, and (d) 53-3Z after heat treatment at 900 °C. These photomicrographs show that little, if any, precipitation products are formed in these alloys during this heat treatment.

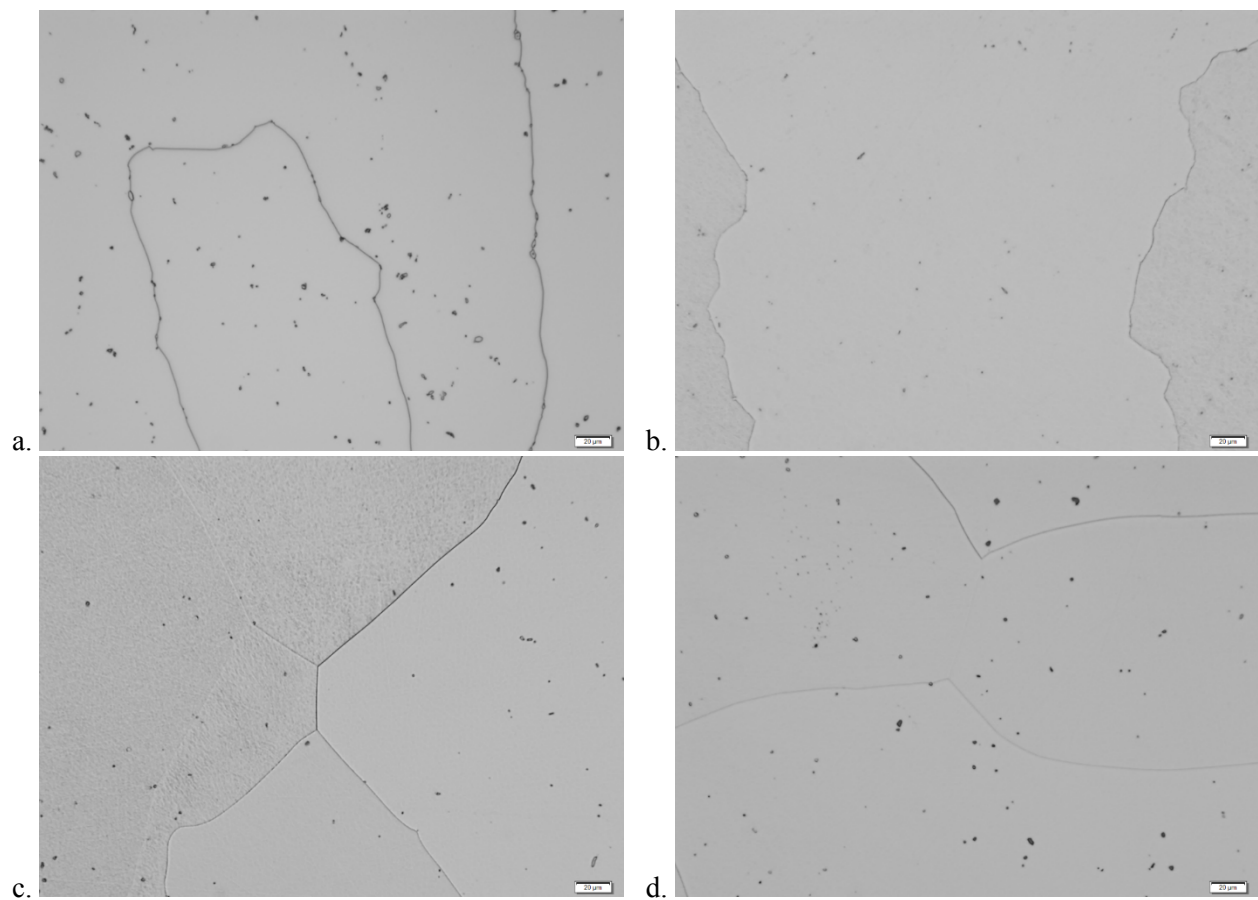


Figure 18.—Photomicrographs showing alloys (a) 53, (b) 53-3T, (c) 53-3H, and (d) 53-3Z after heat treatment at 1,000 °C. These photomicrographs show that little, if any, precipitation products are formed in these alloys during this heat treatment.



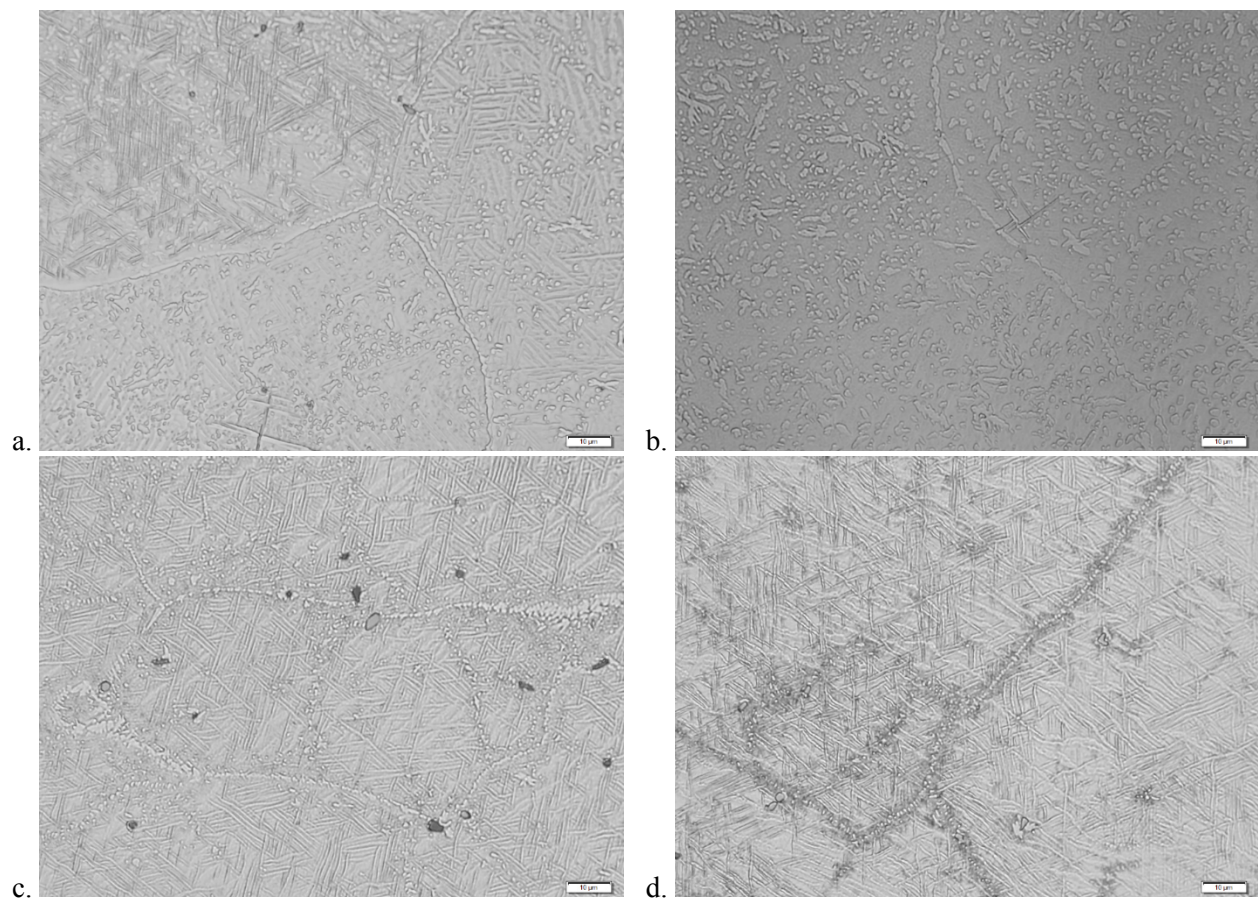


Figure 19.—Photomicrographs showing alloys (a) 54, (b) 54-3T, (c) 54-3H, and (d) 54-3Z after homogenization at 1,050 °C for 48 hr and furnace cooling.

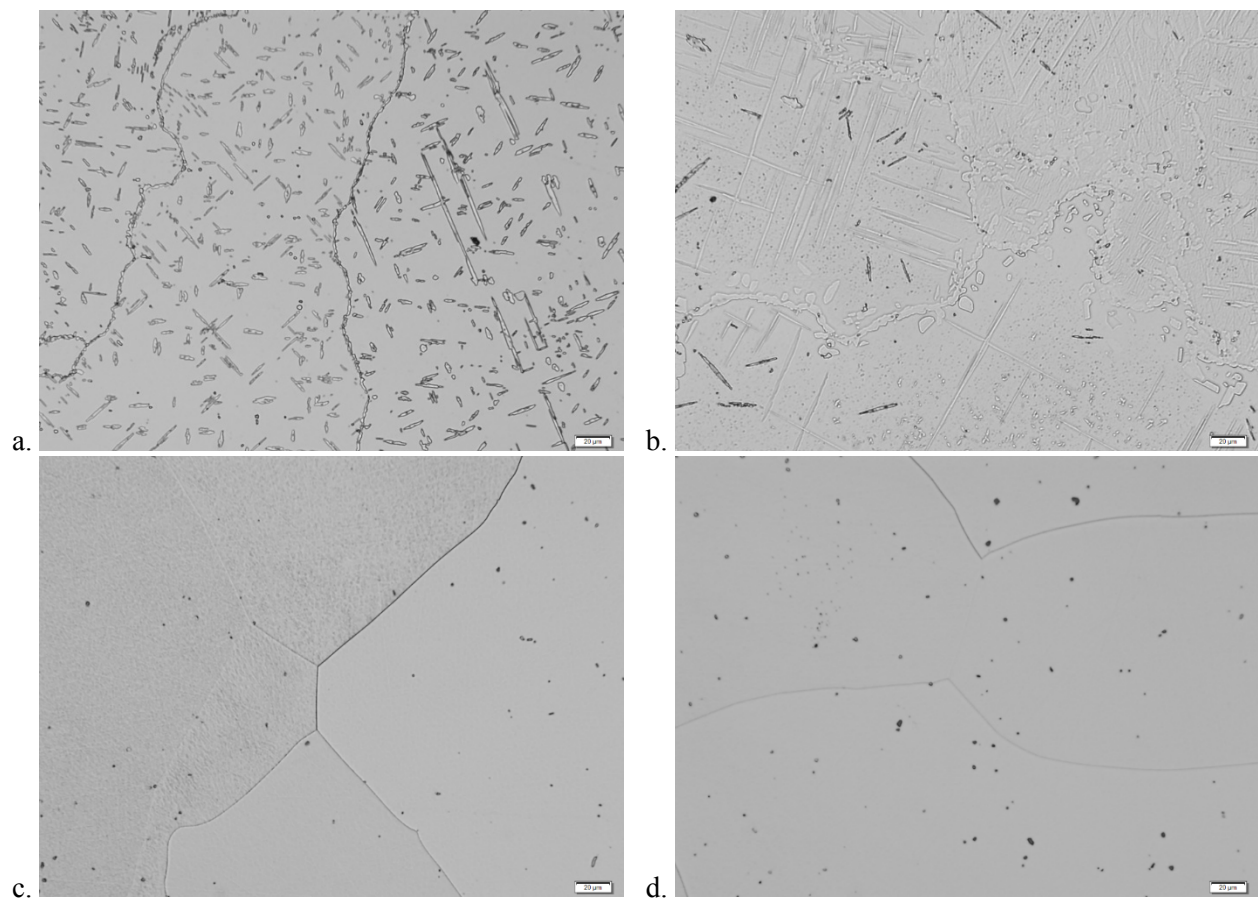


Figure 20.—Photomicrographs showing alloys (a) 54, (b) 54-3T, (c) 54-3H, and (d) 54-3Z after heat treatment at 800 °C. Little, if any, precipitation product is present in alloys 54-3H and 54-3Z (c-d).



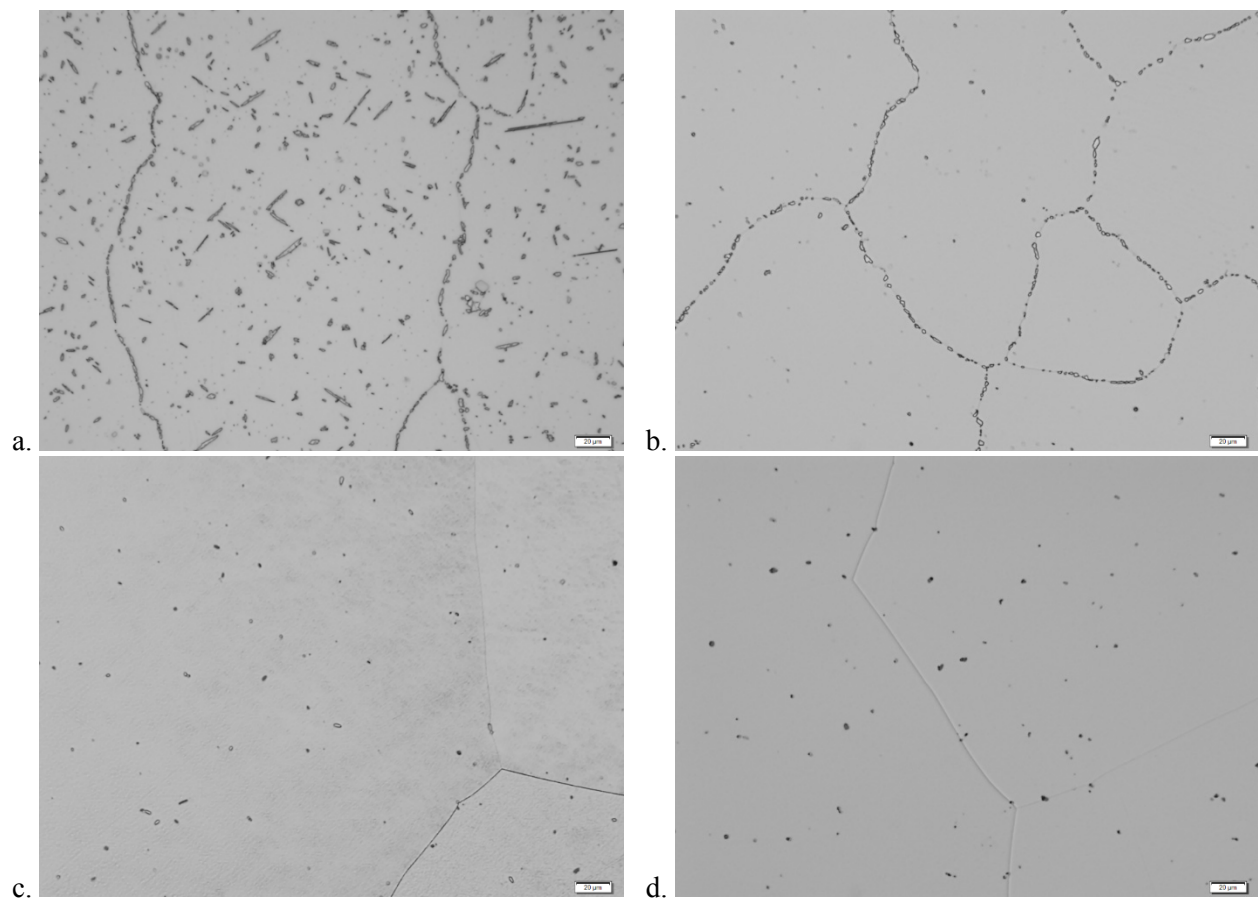


Figure 21.—Photomicrographs showing alloys (a) 54, (b) 54-3T, (c) 54-3H, and (d) 54-3Z after heat treatment at 900 °C. Little, if any, precipitation product is present in alloys 54-3H and 54-3Z (c-d).

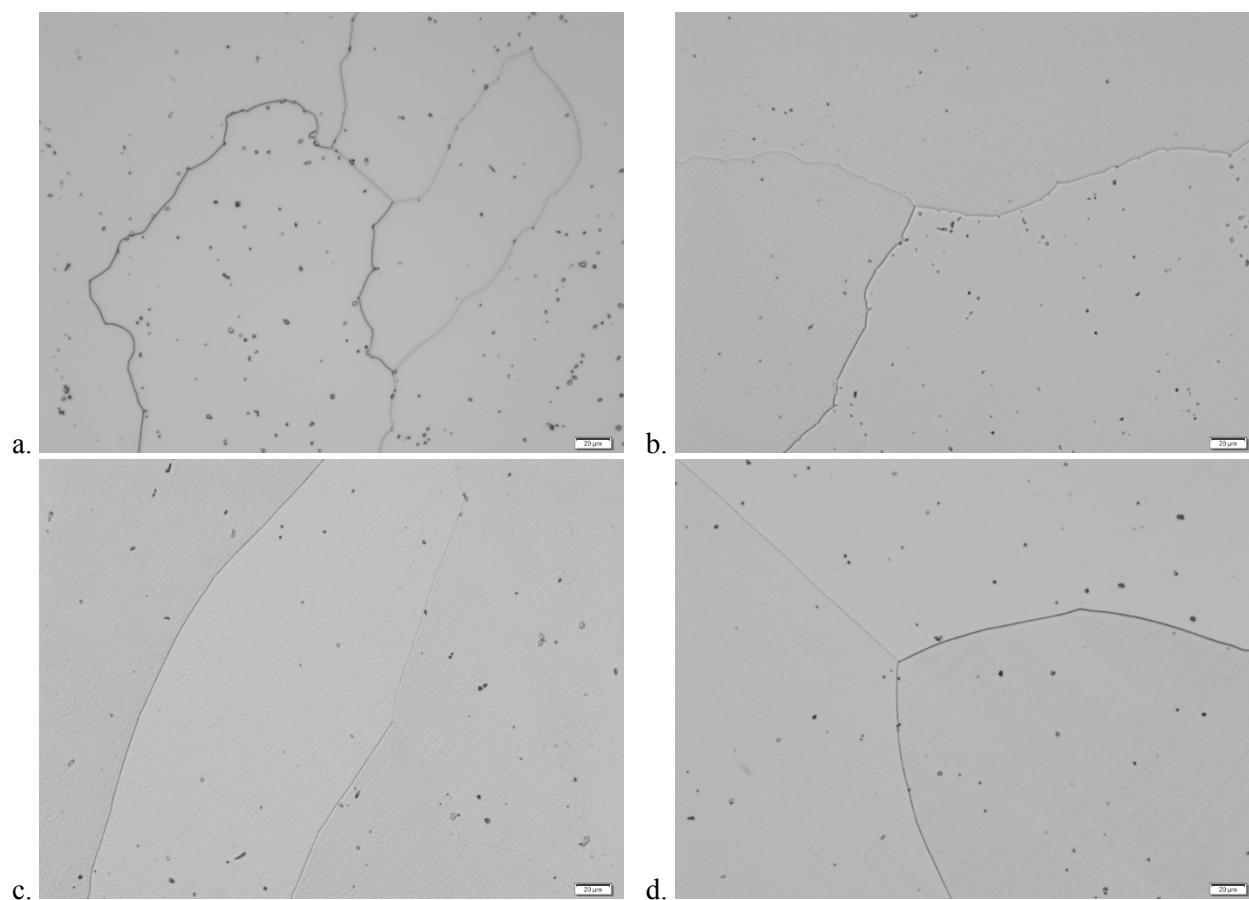


Figure 22.—Photomicrographs showing alloys (a) 54, (b) 54-3T, (c) 54-3H, and (d) 54-3Z after heat treatment at 1,000 °C. These photomicrographs show that essentially no precipitation products are formed in these alloys during this heat treatment.

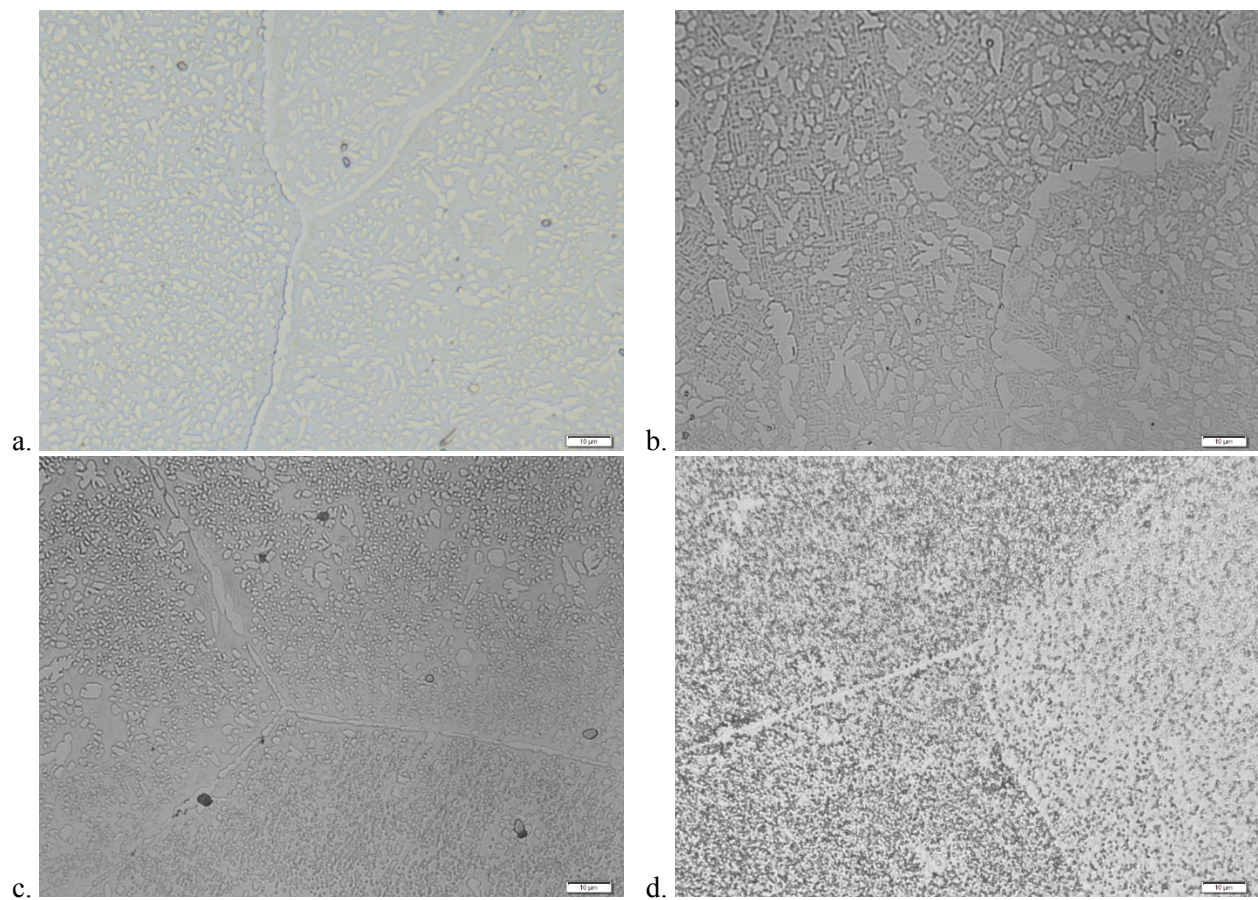


Figure 23.—Brightfield optical photomicrographs showing alloys (a) 55, (b) 55-3T, (c) 55-3H, and (d) 55-3Z after homogenization at 1,050 °C and furnace cooling.

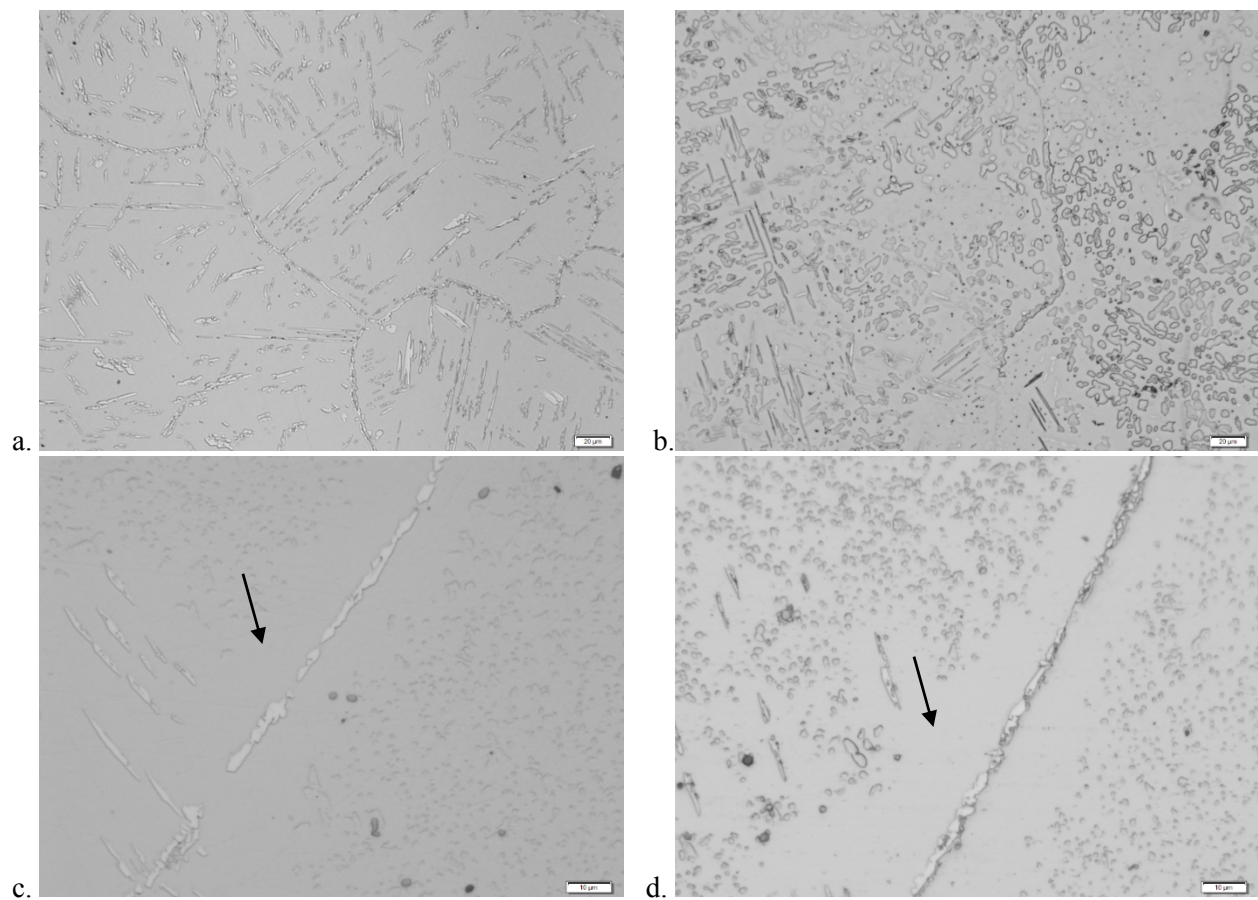


Figure 24.—Photomicrographs showing alloys (a) 55, (b) 55-3T, (c) 55-3H, and (d) 55-3Z after heat treatment at 800 °C. Alloys 55-3H and 55-3Z show denuded zones near the grain boundaries (indicated with arrows).



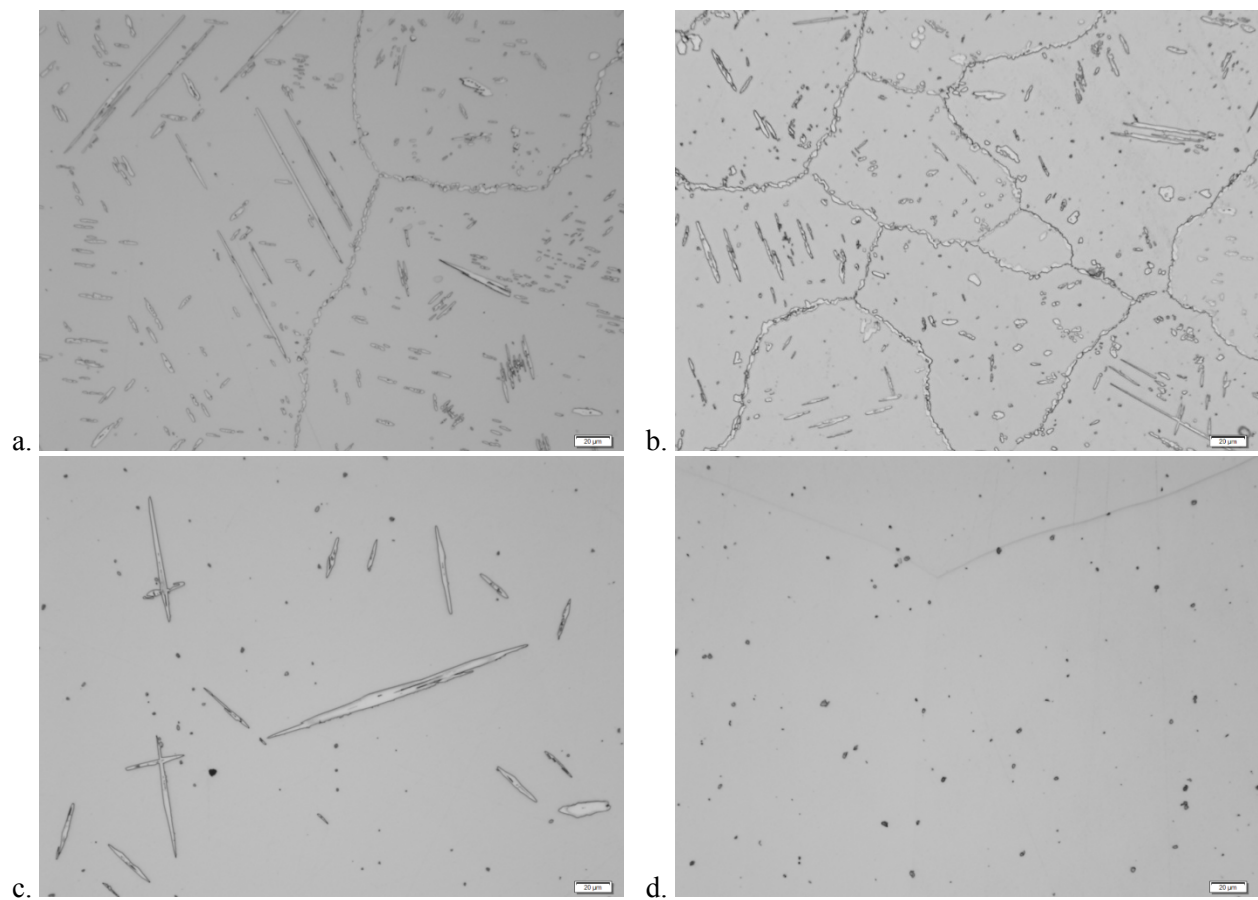


Figure 25.—Photomicrographs showing alloys (a) 55, (b) 55-3T, (c) 55-3H, and (d) 55-3Z after heat treatment at 900 °C. Alloy 55-3Z (d) shows no precipitate formation from this heat treatment.

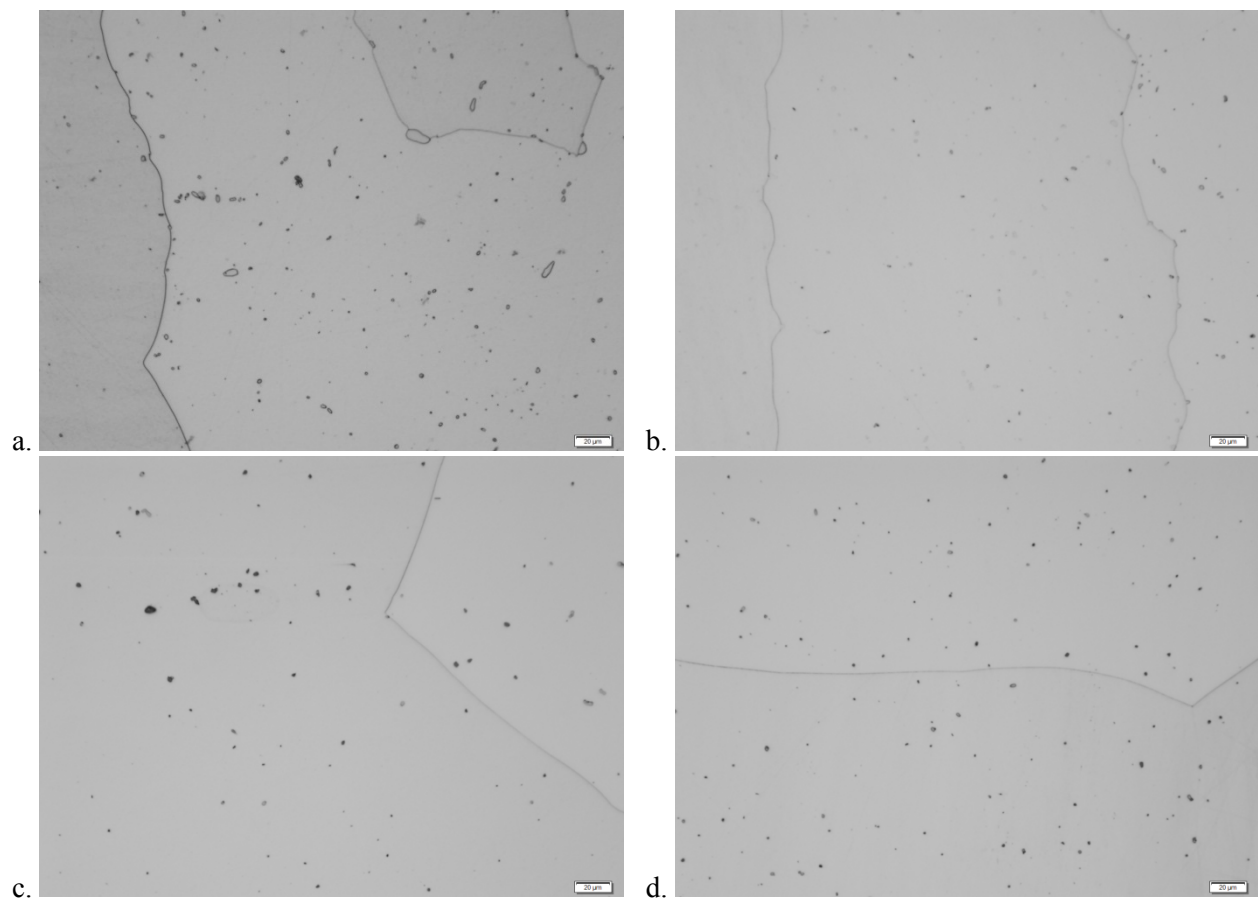


Figure 26.—Photomicrographs showing alloys (a) 55, (b) 55-3T, (c) 55-3H, and (d) 55-3Z after heat treatment at 1,000 °C. These photomicrographs show that essentially no precipitation products are formed in these alloys during this heat treatment.

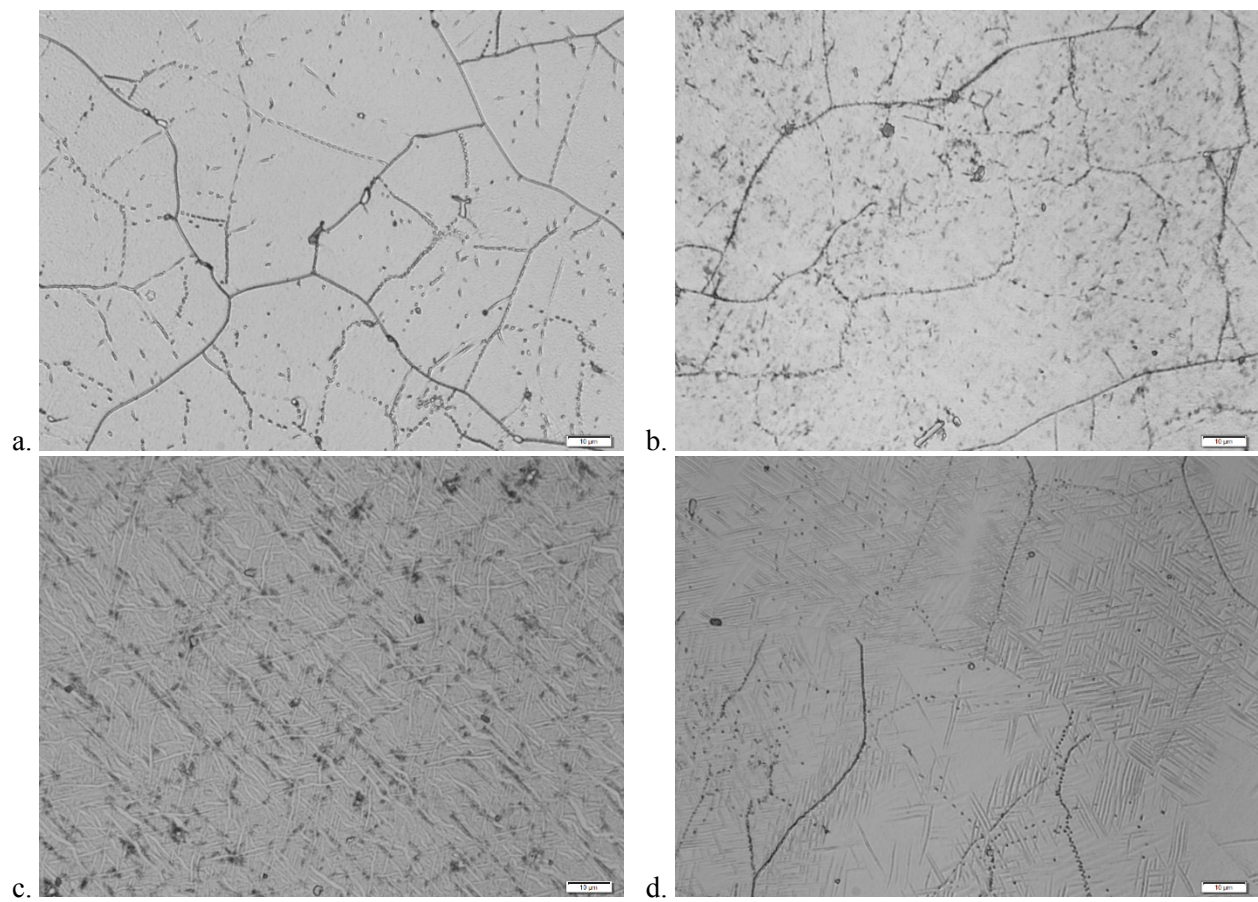


Figure 27.—Photomicrographs showing alloys (a) 52-5H, (b) 53-5H, (c) 54-5H, and (d) 55-5H after homogenization at 1,050 °C for 48 hr and furnace cooling.

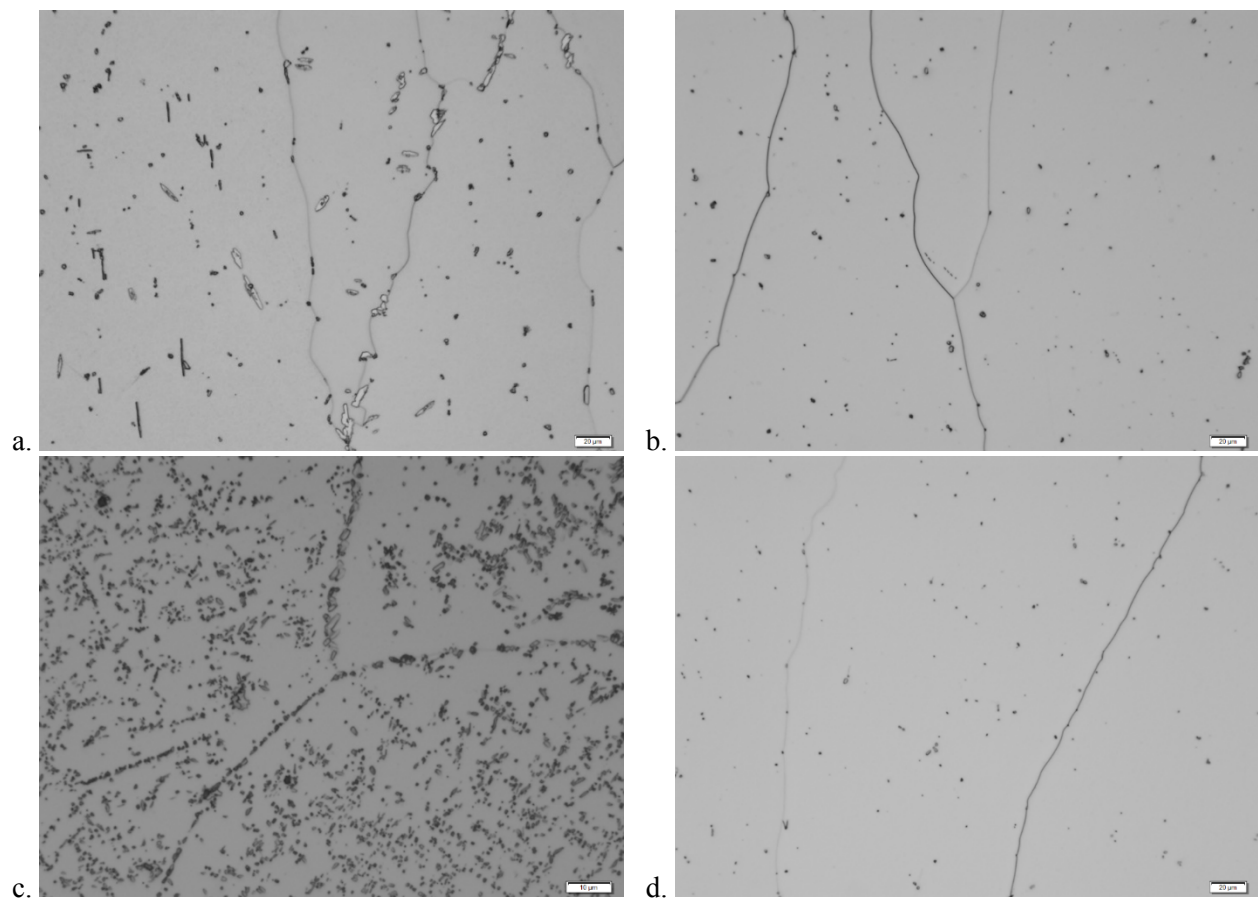


Figure 28.—Photomicrographs showing alloys (a) 52-5H, (b) 53-5H, (c) 54-5H, and (d) 55-5H after heat treatment at 800 °C. Except for alloy 54-5H (c), the microstructures containing 5 at.% Hf had little, if any, precipitation product during this heat treatment.



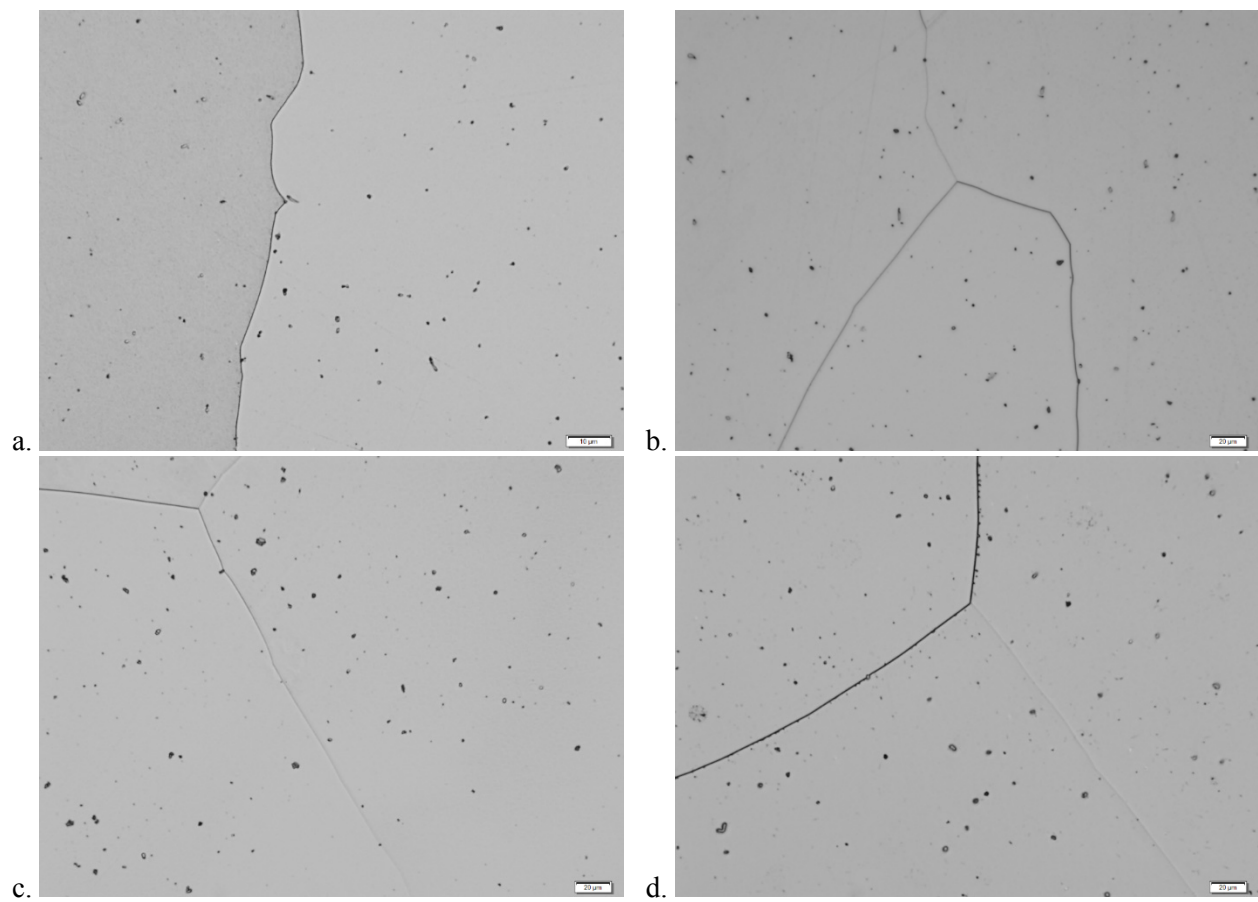


Figure 29.—Photomicrographs showing alloys (a) 52-5H, (b) 53-5H, (c) 54-5H, and (d) 55-5H after heat treatment at 900 °C. These photomicrographs show that essentially no precipitation products are formed in these alloys during this heat treatment.

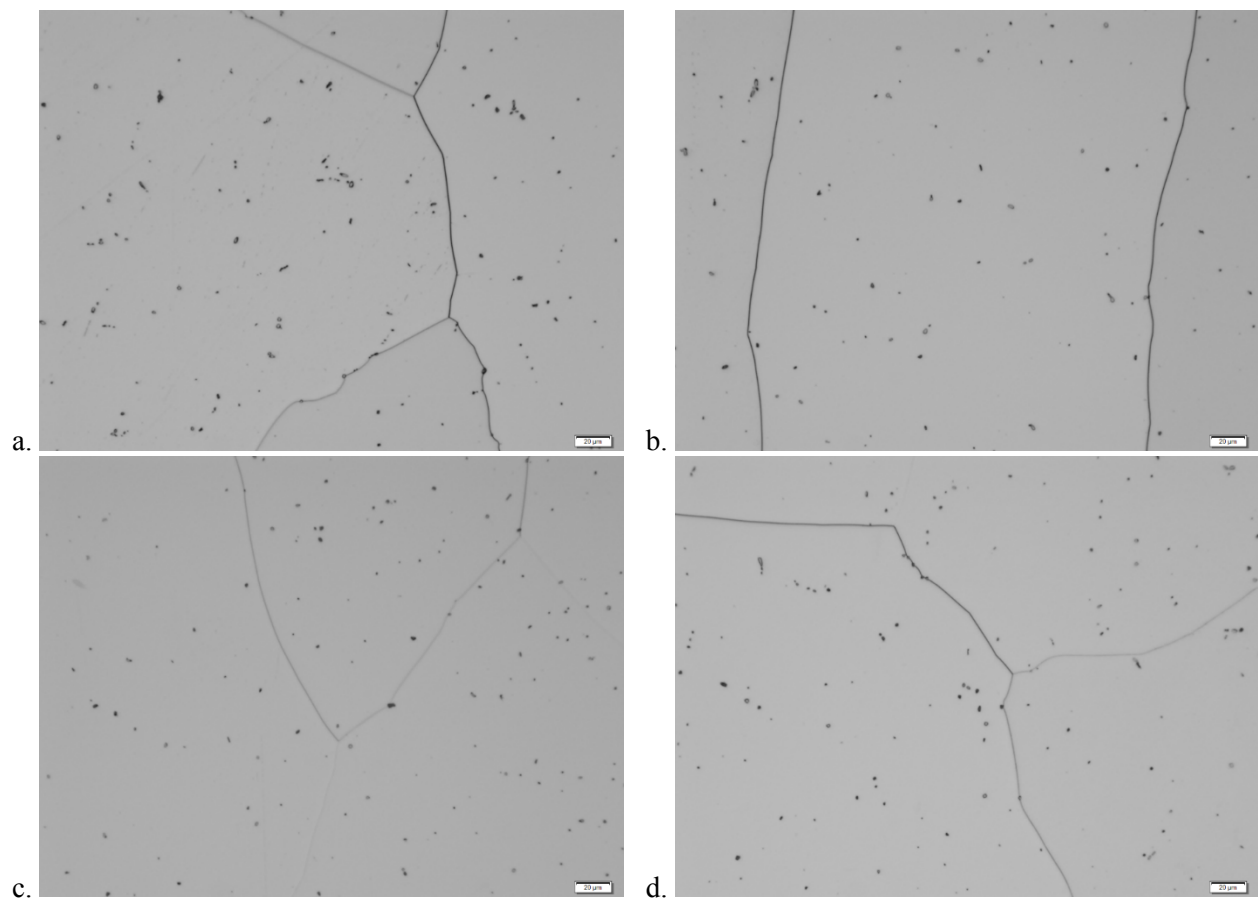


Figure 30.—Photomicrographs showing alloys (a) 52-5H, (b) 53-5H, (c) 54-5H, and (d) 55-5H after heat treatment at 1,000 °C. These photomicrographs show that essentially no precipitation products are formed in these alloys during this heat treatment.

## Second Phase

Figures 31 through 34 show the average second phase volume percent for the studied compounds.

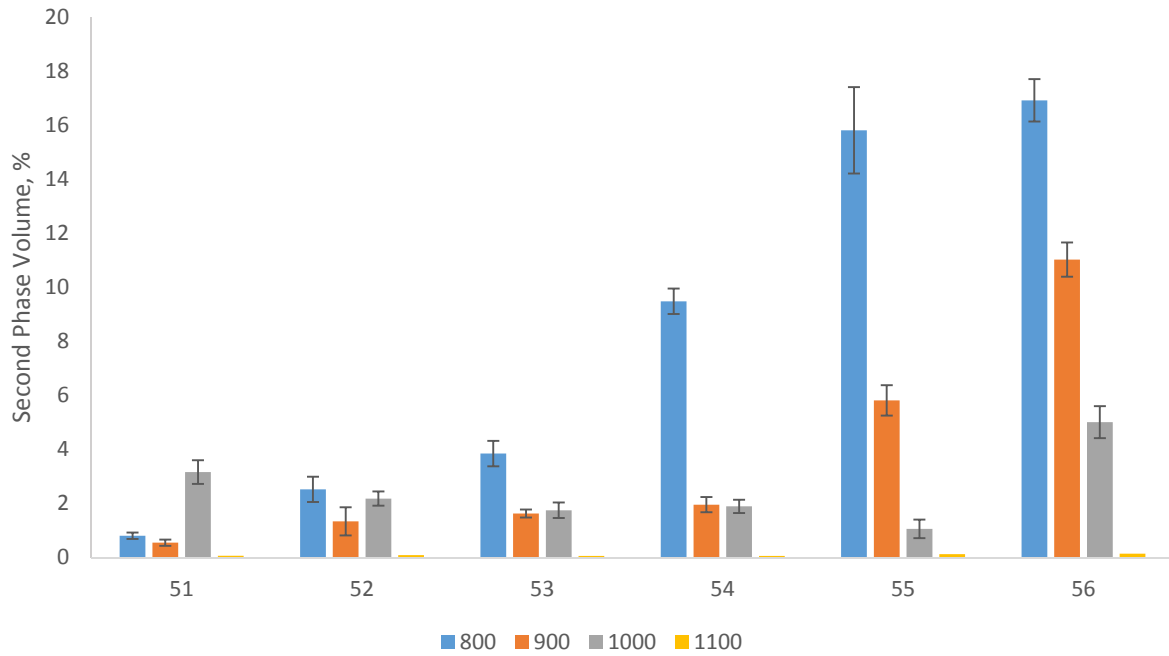


Figure 31.—Second phase volume percent for binary alloys 51 through 56.

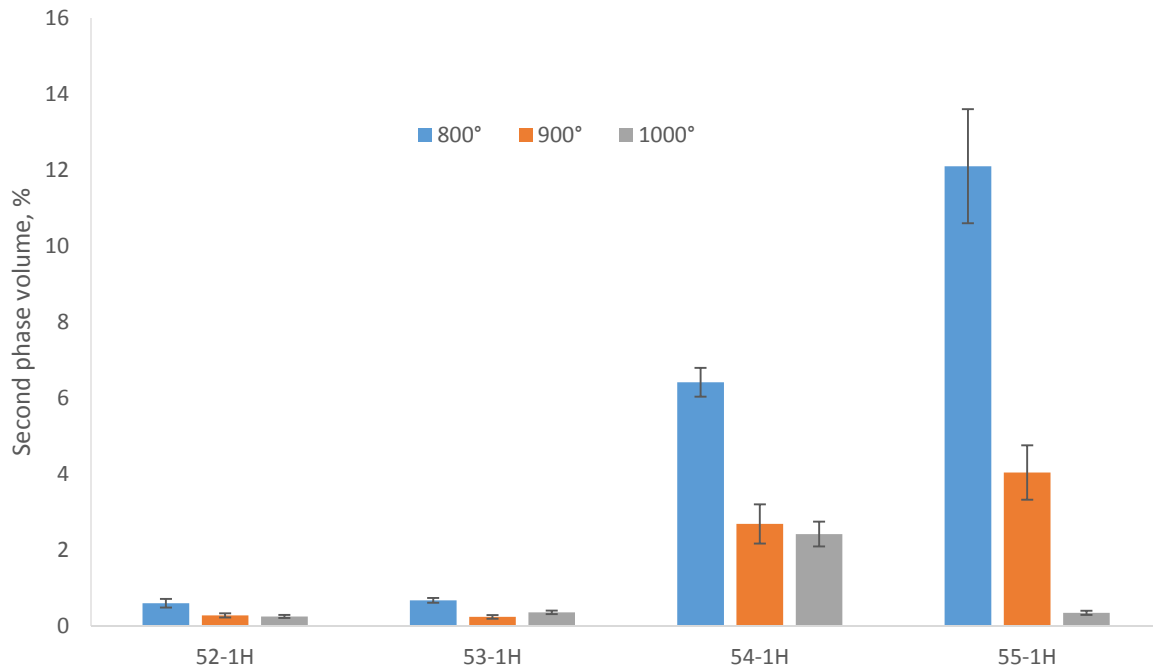


Figure 32.—Second phase volume percent for alloys containing 1 at.% Hf.

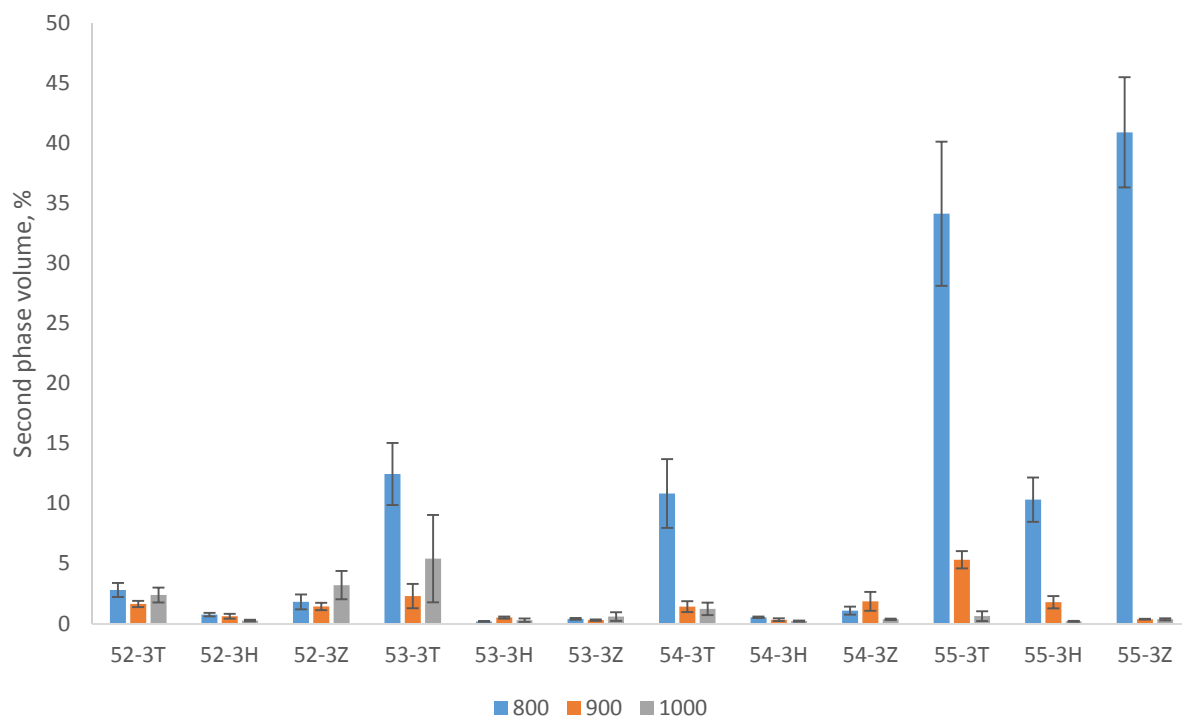


Figure 33.—Second phase volume percent for Ni-Ti-3X alloys, where X is Ta, Hf or Zr.

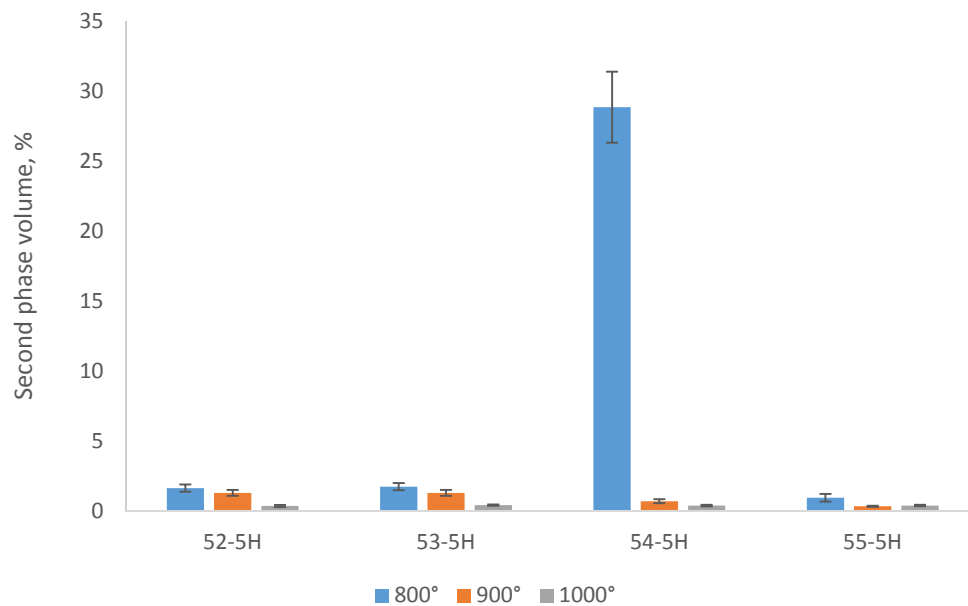


Figure 34.—Second phase volume percent for alloys containing 5 at.% Hf.

## Microindentation Hardness

Figures 35 through 38 show the average hardness measurements for each compound.

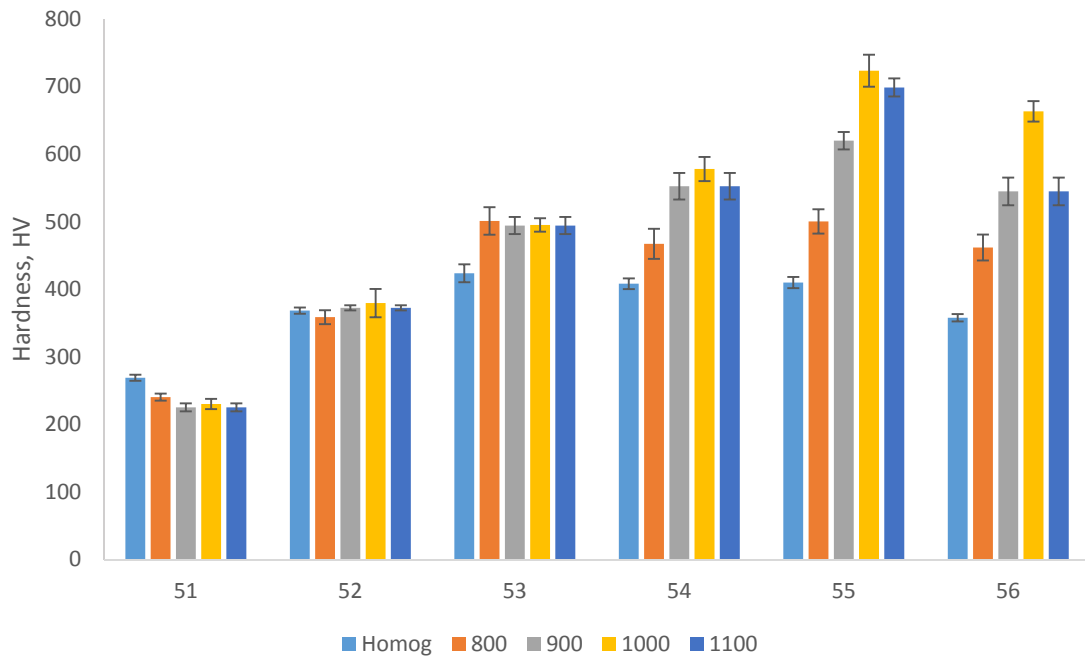


Figure 35.—Hardness for the binary Ni-Ti alloys in this study.

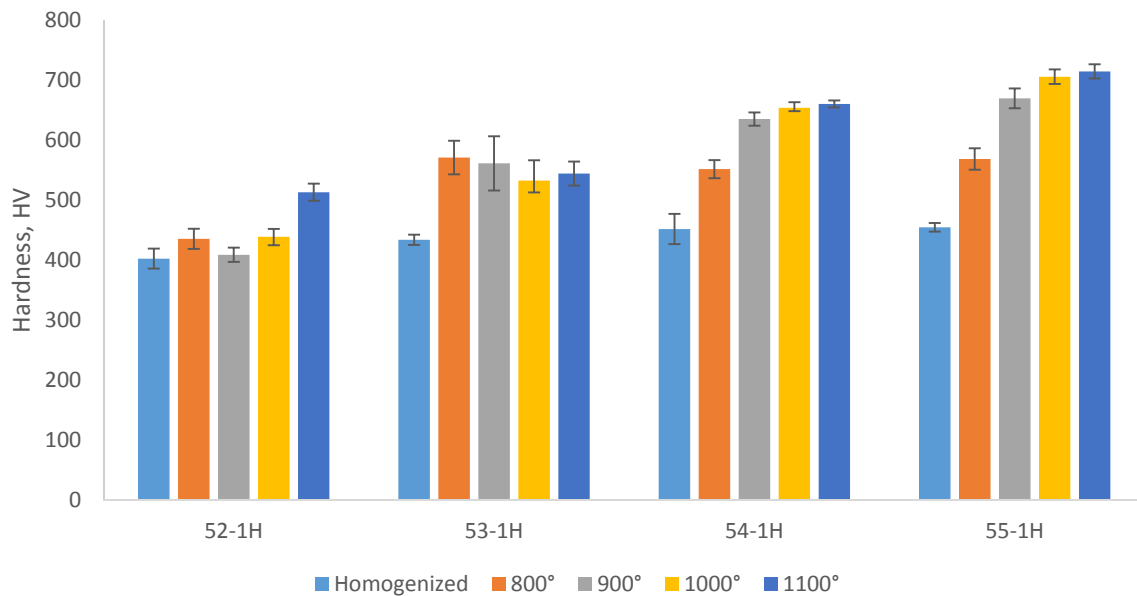


Figure 36.—Hardness for ternary alloys containing 1 at.% Hf.

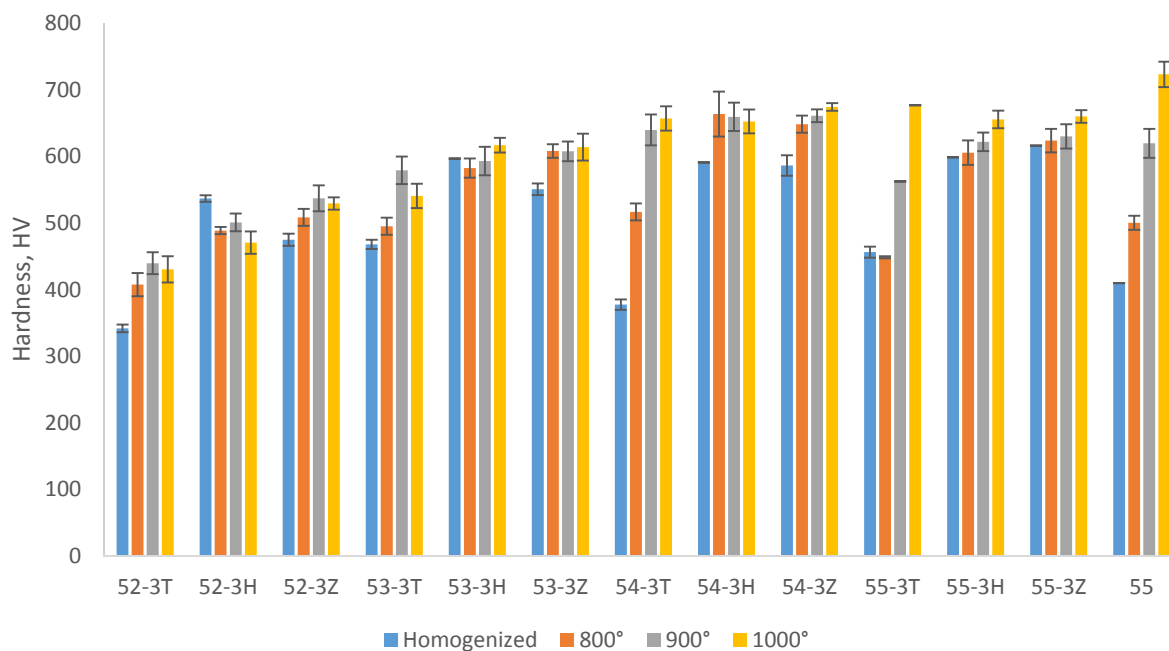


Figure 37.—Hardness of the Ni-Ti-X alloys in this study where X is 3 at.% Ta, Hf or Zr.

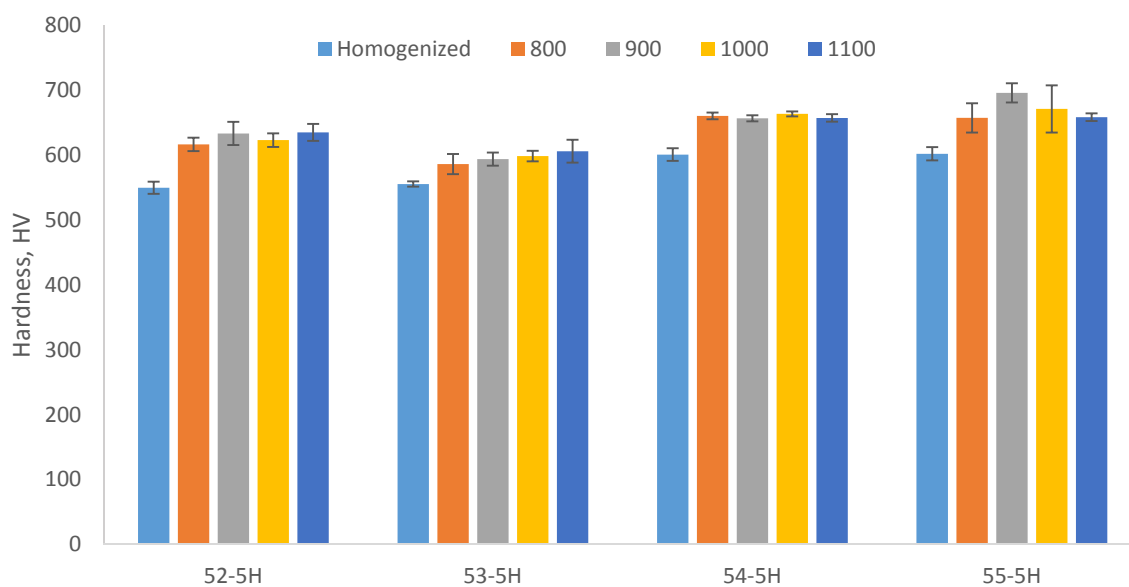


Figure 38.—Hardness of the ternary alloys in this study containing 5 at.% Hf.



## Summary Remarks

This report shows that the highest hardness of the binary Ni-Ti compounds was achieved with alloy 55 (55 at.% Ni – 45 at.% Ti) after heat treatment at 1,000 °C. This heat treatment is somewhat severe and the effect it has on the levels of residual stress in various components is under investigation. After heat treatment at 900 °C, alloy 55 had a hardness of approximately 620HV. This hardness was exceeded when alloys 54-1H, 55-1H, 54-3T, 54-3H, 54-3Z, 54-5H and 55-5H, were heat treated at 900 °C or higher or for alloys 54-3Z, 54-3H, 54-5H and 55-5H even when they were heat treated as low as 800 °C. These heat treatments rendered these alloys with relatively low second phase volume fractions except for alloy 54-5H, which surprisingly had approximately 28 vol.% second phase after the 800 °C heat treatment but essentially no second phase for higher heat treatment temperatures. The exact compositions of the second phase constituents will be identified in detail in future publications. They are generally known to be Ni<sub>3</sub>Ti, Ni<sub>4</sub>Ti<sub>3</sub> and likely other precipitates containing ternary elements that are isostructural with these. The studied compounds may also contain small amounts of oxides and carbides of the ternary elements.

This study also shows that eleven of the studied alloys (namely alloys 54-1H, 55-1H, 53-3Z, 54-3T, 54-3H, 54-3Z, 55-3H, 55-3Z, 52-5H, 54-5H and 55-5H) had hardness values greater than 600HV at heat treatments lower than 1,000 °C. Each of these alloys had less than 5 vol.% second phase, which indicates that the microstructures were relatively free of precipitates that could act as crack initiation sites. This information should be useful to designers interested in bearing-hard materials.

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